

Color Science Notes

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1 Basics of color perception

The way we see color from a painting is complex and involves the biology of the eye, the properties of light, and the properties of the pigment in the paint and it cannot be understood with any of the three left out. This first part covers the eye and our perception of light as color. The ways of describing and measuring color set out here are used in the rest of the paper.

The paint examples throughout come from measurements. Golden has published the reflectance of 78 of its Heavy Body acrylics straight from the tube [24], and Okumura, at the Rochester Institute of Technology, measured 26 matching colors from Golden's Matte Fluid line mixed with more and more white [59]. Those 26 are the calibrated paints of this paper. Most mixtures shown here are computed from them with a model of how paint handles light, built on Okumura's measurements and explained in Section 2.6; the other 52 paints appear only as the colors Golden measured.

1.1. The light spectrum. Light travels as a wave, and the length of the wave, the distance from one crest to the next, decides what color the light looks when it is seen on its own. Visible wavelengths are tiny, so they are measured in nanometers, millionths of a millimeter. A light source emits a mixture of wavelengths. The eye can see wavelengths from about 380 to about 780 nanometers, with almost all of the useful range between 400 and 700 nanometers, and a single wavelength seen alone has a definite color, running from violet at the short end through blue, green, yellow and orange to red at the long end. Ordinary white light, from the sun or a generic lamp, contains all of them at once but at varying strengths.

A surface changes the mixture by sending back some fraction of the light at each wavelength and absorbing the rest. The curve that gives that fraction for every wavelength is the surface's reflectance curve. It is the physical fact behind the surface's color, and the color itself is what the eye makes of the curve. A yellow paint sends back most of the light from the green to the end of the red and absorbs the blue and violet. A blue paint does the reverse.

What reaches the eye depends on the light as well as the paint. At each wavelength the paint sends back its share of whatever arrives, so the same paint sends a different mixture of light to the eye in daylight than under a tungsten bulb. Color scientists describe a light source by how much light it gives at each wavelength, and they call the standard ones, set by the CIE, the international body for color standards, illuminants. Figure 1(b) compares two of them. Daylight is nearly even across the spectrum, while tungsten light is weak in the blue and several times stronger at the red end, so a tungsten-lit room looks orange next to daylight. How the eye still sees a paint as roughly the same color under both is the subject of Section 1.5.

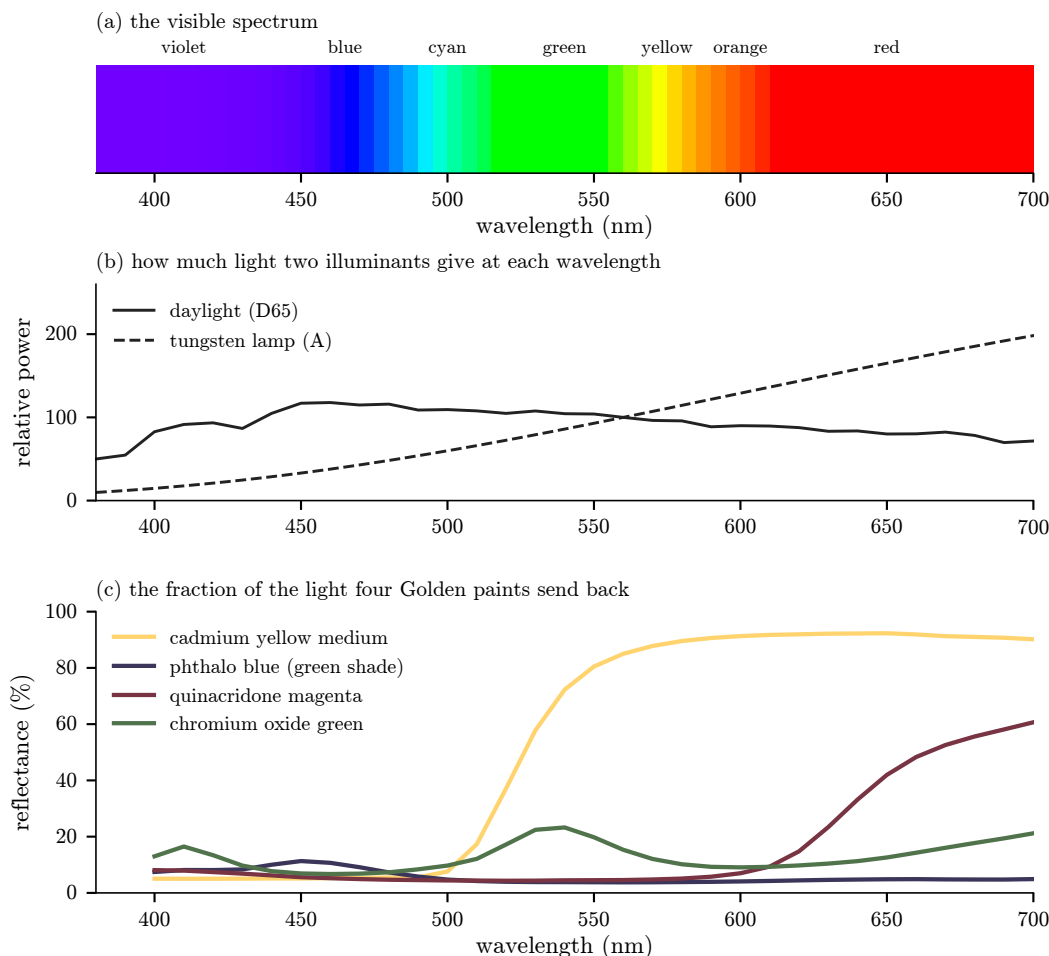


Figure 1: (a) The visible spectrum: the color each wavelength has when it is seen alone, with the usual names of the regions. (b) How much light daylight (the CIE’s standard daylight, D65) and a tungsten illuminant (the CIE’s illuminant A) give at each wavelength, both scaled to 100 at 560 nm. (c) The reflectance curves of four Golden Heavy Body acrylics, the share of the light each one sends back at each wavelength [24].

The four curves in panel (c) belong to Golden Heavy Body acrylics, measured by Golden on a layer of paint spread over a white card [24]. Painters call paint used straight from the tube, in a layer like this, its *masstone*, and paint mixed with white a *tint*. Cadmium yellow medium reflects almost none of the violet and blue light and more than nine tenths of everything from yellow to red. Phthalo blue reflects only about a tenth of the light even at its peak in the blue, so straight

from the tube it looks nearly black. Quinacridone magenta reflects the red end strongly and the violet end a little, with very little in between. Chromium oxide green reflects a modest band of green and nearly as much deep red, but the eye is so insensitive to deep red that the red hardly shows.

One detail in these curves matters later. In Golden's measurements none of the dark paints reads less than about 4 percent at any wavelength, because their instrument collects the light that bounces off the top surface of the paint, before it ever gets in, along with the rest. That surface reflection is much the same at every wavelength, so in these measurements it adds a little of the illuminant's own light, unchanged, to every color. The light that carries the paint's color is the part that gets past the surface, into the paint, and back out again (Section 2.2).

1.2. The three kinds of cone. The retina, the light-sensitive layer at the back of the eye, does not record the reflectance curve. It has three kinds of cone cell, and each kind responds to a broad range of wavelengths that overlaps with the ranges of the other two. A cone simply counts the light it absorbs. It cannot tell which wavelength the light had, so a lot of light at a wavelength it is not very sensitive to gives the same signal as a little light at its favorite one. All the eye ever learns about a patch of color is therefore three numbers: how strongly the patch excites each kind of cone. However complicated the reflectance curve, the eye reduces it to those three numbers, and every color we can see is a particular combination of them.

The three kinds are named for where their sensitivity peaks: long-wavelength or L cones in the yellow-green, middle-wavelength or M cones in the green, and short-wavelength or S cones in the blue-violet. They are often called red, green and blue cones, which is misleading, since the L cones peak in the yellow-green and all three respond over wide ranges. Figure 2(a) shows how sensitive each kind is at each wavelength, from the measurements of Stockman and Sharpe that the CIE has adopted as its standard [70, 12]. The curves are broad and the L and M curves overlap almost completely, so no wavelength excites only one kind of cone.

Panel (b) gives the three signals for four paints in daylight, each as a share of what a perfect white would produce. Cadmium yellow medium excites the L and M cones strongly and the S cones hardly at all, and that combination is what the eye sees as a light, vivid yellow. Phthalo blue straight from the tube gives all three very little, with the S cones slightly ahead: a very dark blue. Chromium oxide gives three similar, low signals with the M cones a little ahead, which the eye reads as a dull, dark green.

The eye also has rods, which handle vision in dim light and play no part in the colors a painter sees. The three kinds of cone are far from equal in number. Only about one cone in twenty is an S cone [17, 18], and the ratio of L to M cones varies enormously from one person to another, from about one to one to more than sixteen to one in a study of people with normal color vision [33]. People with very different mixes of cones still see much the same colors, because the later stages of vision calibrate themselves to whatever cones they are given.

Because the eye works with three numbers, color can be measured with three numbers. In 1931 the CIE defined a standard way to compute three such numbers from a reflectance curve and an illuminant, and they carry very nearly the same information as the three cone signals. One of them, called Y, is the share of the light the surface sends back, counted the way the eye counts it, and it sets how light the color looks. Every color calculation in this paper starts from these three standard numbers, and the appendix to this part (Section 1.9) gives the formulas.

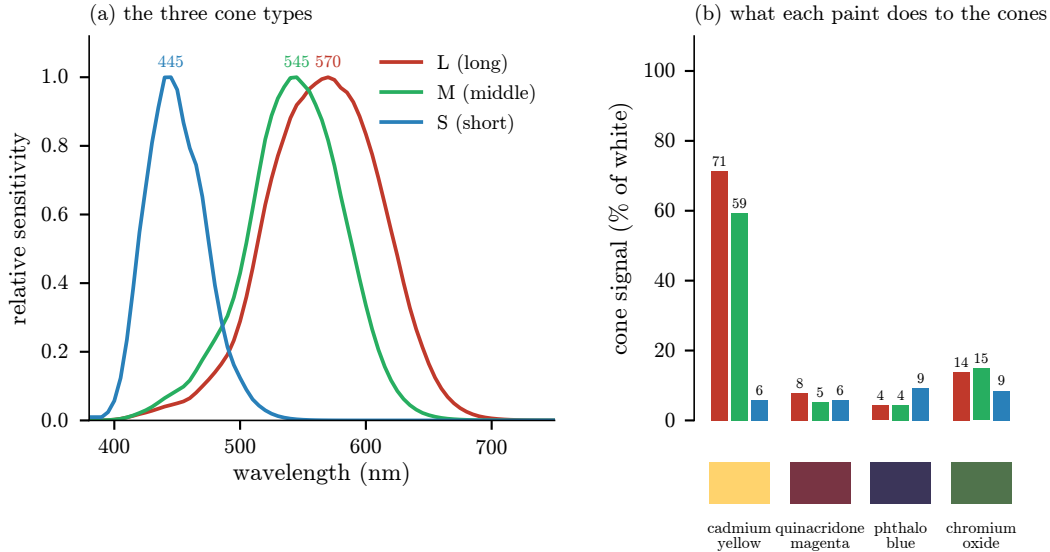


Figure 2: (a) How sensitive each of the three kinds of cone is at each wavelength, from Stockman and Sharpe [70], each scaled to its own peak; the peaks are marked. (b) The signal each kind of cone receives from four Golden paints in daylight, as a percentage of what it receives from a perfect white.

Working from three signals also means that two different spectra giving the same three look identical, the subject of Section 1.4. And no single wavelength of light is “pure” in any sense the cones recognize, since every wavelength excites at least two kinds of cone.

1.3. The opponent process. The three cone signals are not what we experience. Before they leave the retina they are recombined into three new signals: one for light against dark, one for red against green, and one for blue against yellow. Each of the two color signals can swing one way or the other but not both at once. So there is no reddish green and no bluish yellow, and there are exactly four hues that look like nothing but themselves: a red that is neither orange nor purple, a yellow that is neither greenish nor orange, a green, and a blue. The rest of the brain’s work on color, in the visual cortex, builds on these three channels. The arrangement explains why yellow, which comes from the long and middle cones together, feels like an elementary color, and why the color spaces used for measuring paint are built around a red-green axis and a yellow-blue axis.

Those four hues are called the unique hues, and they can be pinned down by experiment. Hurvich and Jameson asked observers to cancel the redness, greenness, yellowness or blueness of a light by adding some of the opposite hue, which let them find where each color channel falls silent. A blue with no trace of green or red, a green that is neither yellowish nor bluish, and a yellow that is neither reddish nor greenish each turned up at a single wavelength of the spectrum, near 475, 500 and 577 nm [35]. Later studies of many observers agree to within a few nanometers, with about as much spread from one person to the next [65]. No single wavelength gives a unique red: a red that is neither orange nor purple needs a little violet light added to a long-wavelength red.

The channels are drawn in Figure 3(a) for light of one wavelength at a time. Each color curve rises above zero for one hue of its pair and falls below zero for the other. The red-green channel

leans to red at both ends of the spectrum and to green in the middle, so violet light looks a little reddish. The yellow-blue channel leans to yellow over the middle and long wavelengths and to blue at the short end. Where the red-green curve crosses zero, the light has no redness or greenness and looks purely yellow or purely blue; where the yellow-blue curve crosses zero, it looks purely green. The dotted lines mark these unique hues as the experiments found them. In panel (b) the same four paints as before are broken into the three channels. Cadmium yellow sends a strong yellow signal and hardly any red or green. Phthalo blue sends a blue one with little red or green, chromium oxide a dark green tinged with yellow, and quinacridone magenta, straight from the tube, a red with little yellow or blue.

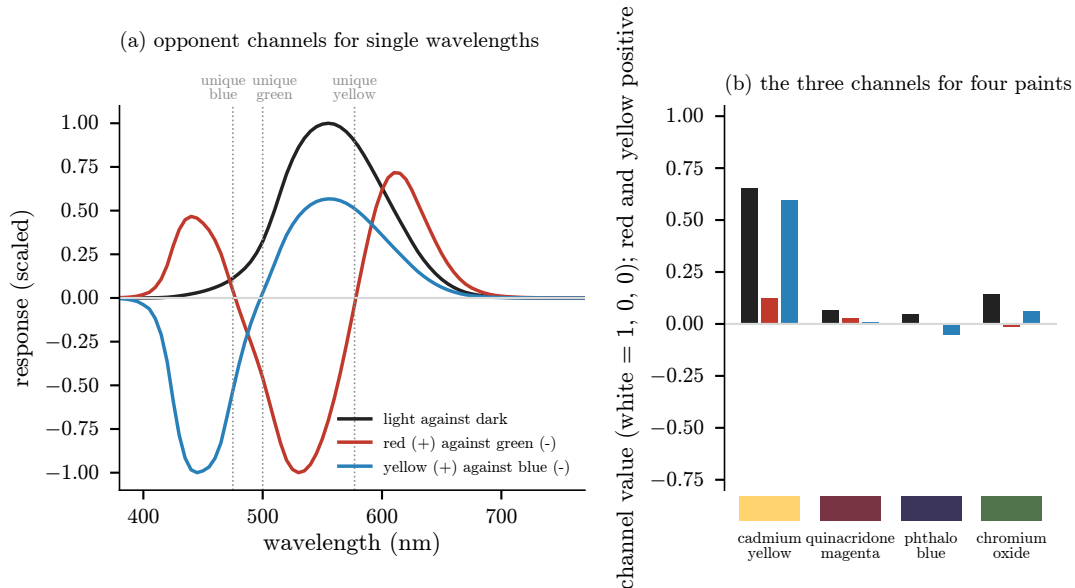


Figure 3: (a) The three opponent channels for light of one wavelength at a time: light against dark, red against green, and yellow against blue, each scaled to its largest value. The dotted lines mark the unique hues at 475, 500 and 577 nm, where the channels measured in experiments cross zero [35]. (b) The three channels for four paints in daylight, scaled so that a white gives full lightness and no color.

Hering proposed the opponent process in 1878, from the look of colors alone: no color ever looks both red and green, or both yellow and blue [32]. His idea long seemed to compete with the theory of Young and Helmholtz that the eye has three kinds of receptor, until Hurvich and Jameson showed in 1957 that the two fit together, with three kinds of cone at the front and opponent channels built from their signals behind [35]. Cells in the retina that compare the cones in just these ways have since been found [19]. Further on, in the visual cortex, cells compare the color of each patch with the colors around it [79], and our sense that a surface’s color belongs to the object, and stays with it when the light changes, is built from those comparisons.

The two color channels also explain why the hues form a circle. Hue runs red, yellow, green, blue and back to red through the purples, because every hue is a direction in the plane of the red-green and yellow-blue signals, and going all the way round brings you back to where you began. The purples are not in the spectrum at all. A surface looks purple only by sending both color signals toward red and blue at once, which means reflecting both ends of the spectrum and

absorbing the middle. Quinacridone magenta's curve in Figure 1(c) has that shape, but straight from the tube its violet is too weak to count and it reads as a red; with white it moves toward magenta (Section 3.3).

Yellow's special place comes from the channels too. To the cones yellow is nothing special, a roughly equal excitation of the L and M cones with almost none of the S, but to the opponent channels it is one end of an axis, as basic as red, green or blue, and that is the level at which we name colors. Red, yellow, green and blue are the four primaries of perception. Part 4 shows that they are not the primaries of mixing paint.

1.4. Metamers. Because the eye reduces every spectrum to three numbers, many different spectra give the same three numbers and look identical. Two surfaces with different reflectance curves that match under one illuminant are called metamers, and a painted copy of a color is almost always a metamer of the original, not a copy with the same curve. The catch is that the match holds only for the illuminant it was made under. Change the illuminant and the two curves are weighted differently, and the match can break. This is why a mixed green that matches a tube green in daylight can part company with it under fluorescent light, and why a color matched in the studio can look wrong in the gallery.

Figure 4 shows such a pair made from Golden paints. The target is chromium oxide green, a single pigment. The match is a mixture of hansa yellow medium, ultramarine blue and titanium white, worked out with the mixing model to look as much like the chromium oxide in daylight as three paints can. The two reflectance curves are plainly different: the mixture reflects more blue-green light and much less deep red. In daylight the two colors differ by about one unit of color difference. One unit is about the smallest difference a careful observer can see with two colors side by side. Under a tungsten illuminant they still match for most purposes, because tungsten light changes smoothly across the spectrum and treats the two curves in much the same way. Under the fluorescent illuminant F11, whose light comes in three narrow bands, they differ by about five units, which anyone can see: the bands happen to fall where the two curves are far apart.

Whether a match survives a change of light depends on how its two curves differ. Where they cross several times and stay close together, the small differences cancel under any light that changes smoothly across the spectrum. The mixture here crosses the chromium oxide curve four times and lies close to it through the blue, and so it survives tungsten well. Two curves that differ in one broad band are more fragile, since any light that is strong in that band will expose them. People differ, too. The eye's sensitivity varies a little from person to person, with age, the yellowing of the lens and inherited differences in the cones, so a pair that matches for one person may not match for another [20]. This is called observer metamerism. A match is best judged by more than one person for this reason, and the CIE's standard observer, the set of sensitivities used in every color calculation, is an average over many people.

A mixed match is therefore a metamer of its target, and the wider the range of light it will be seen under, the more it matters that its reflectance curve resembles the target's as well as its color. A match made with pigments like the target's, which is to say with a similar curve, is safer than one made with unrelated pigments. Computer matching, in Section 3.11, reports a measure of how far a match drifts under other light, the index of metamerism, alongside the recipe. The exact condition for a match, and how much freedom the curves that share one color have, are in Section 1.9.

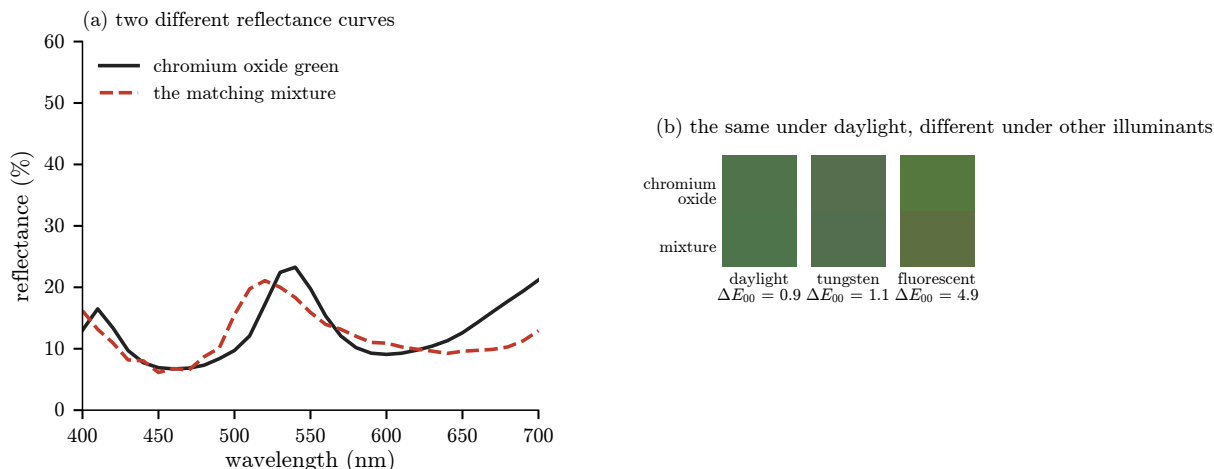


Figure 4: A metameric pair. (a) The reflectance curves of chromium oxide green and of a mixture of hansa yellow medium, ultramarine blue and titanium white chosen to match it in daylight. (b) The two colors in daylight, under a tungsten illuminant and under the narrow-band fluorescent illuminant F11, with the color difference between them under each.

1.5. Adaptation. The light reaching the eye from a white sheet of paper is orange under a tungsten illuminant and bluish in the shade of a clear sky, yet the paper looks white in both. The visual system corrects for the color of the light by rescaling the three cone signals so that whatever is lighting the scene comes out neutral. The correction is nearly automatic and good, but not perfect: a vivid red looks somewhat different under tungsten light than in daylight even after the eye has adapted. The rescaling is set by the white, which sends back every wavelength. A red paint sends back only the long end of the spectrum, where tungsten’s extra light is greatest, so it gains more from the tungsten than the white does, and the correction cannot take all of that gain away.

The top row of Figure 5 shows seven Golden paints as they look in daylight. The middle row is the light they send back under a tungsten illuminant before any adaptation: everything has gone orange, the white included, which is what a camera with its white balance fixed for daylight would record. The bottom row imitates the eye’s correction by scaling three cone-like signals until the white comes out white again, a rule first proposed by von Kries. Most of the paints return close to their daylight colors, the white and yellow ochre to within less than two units of color difference. The reds and the deep green do not quite make it, and pyrrole red is still about five units away. The reds stay lighter and more orange, for the reason just given, while the green has lost some of the little blue light it had. The leftover change is called color inconstancy. It comes from the paint’s reflectance curve, and it is largest for vivid colors whose curves are least like the white’s.

The correction takes time and is not complete. Most of it happens within a few seconds and the rest over a minute or two, and observers adapt most of the way to a colored light but not all of it, so a tungsten-lit room keeps a faint warmth even after a long stay [23]. The same correction also works on small parts of the visual field. Stare at a red patch and the L cones in that part of the retina turn down their sensitivity; look away at a white wall and the white looks greenish, which is the afterimage. A gray patch surrounded by a vivid color shifts toward the opposite hue,

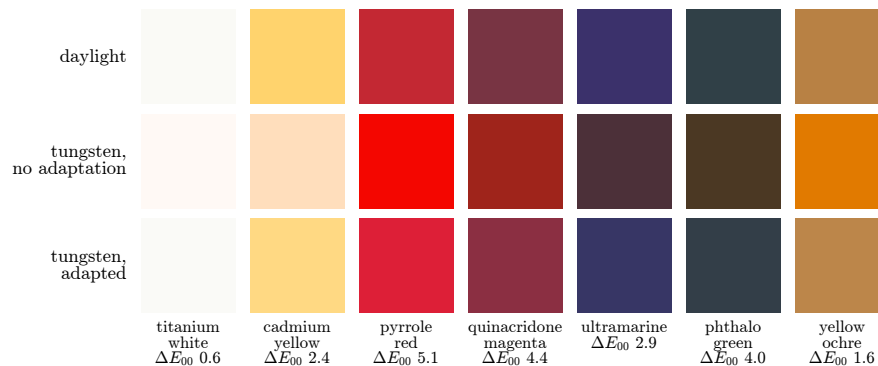


Figure 5: Adaptation to the color of the light. Top: seven Golden paints in daylight. Middle: the same paints under a tungsten illuminant, with no adaptation. Bottom: under tungsten after a correction of the kind the eye makes, rescaling three cone-like signals so the white is white again. The number under each column is the color difference between the corrected tungsten color and the daylight color: the part of the change that adaptation does not undo.

by a related mechanism that compares each region with its neighbors. These effects are large in a painting, where the “light” around a patch is whatever the painter has put there, and a mixed gray that measures neutral can look warm or cool depending on its neighbors. Measurements in this paper are all for isolated patches under daylight.

1.6. The six attributes of color. When we describe a color we are describing three things at once: which hue it is, how light it is, and how vivid it is. CIE names these carefully, and it names six attributes rather than three, because there are different ways to describe how light and how strong the color is. Brightness is how much light a thing seems to give off; lightness is its brightness compared with a white in the same light. Colorfulness is how much color a thing seems to have; chroma is its colorfulness compared with a white in the same light. Saturation is colorfulness compared with the thing’s own brightness. Hue is the one attribute with no partner. The distinction matters because a red car is the same red in sunlight and in shade: its brightness and its colorfulness fall in the shade, its lightness, chroma and hue do not, and lightness, chroma and hue are what we mean when we say what color a thing is. The relative versions hold steady because of adaptation (Section 1.5): the visual system rescales its signals to the light it is in, so the ratio of a surface’s signal to the white’s stays nearly the same as the light gets brighter or dimmer, and that ratio is what lightness and chroma report. A paint has a lightness, a chroma and a hue; its brightness and colorfulness depend on the light it is seen in. Saturation is a property of both light and surfaces. It compares a color only with its own brightness, so it needs no white beside it, and it applies as well to a light seen alone in the dark as to a paint. The CIE’s exact wording for all six is collected in Section 1.9.

CIELAB, the next subsection, provides only hue, value and chroma, which is all a surface color needs; when saturation is wanted, chroma divided by lightness is used. Painting manuals use *saturation*, *intensity* and *chroma* as one word. Of the three, chroma is nearly always what is meant, since a painter judging a paint on the palette is comparing it with the white beside it. The rest of this paper uses chroma, lightness or value, hue, and saturation in the CIE’s senses. Where it calls a paint vivid, in the everyday sense, any number given is its chroma.

1.7. Color spaces, and CIELAB in particular. To talk about mixing precisely we need coordinates for color. The ones used throughout this paper are CIELAB. Lightness (L^*) runs from 0 for black to 100 for white. Two color coordinates run across it, one from green to red (a^* , negative for green and positive for red) and one from blue to yellow (b^* , negative for blue and positive for yellow), and a gray sits at zero on both. A color's distance from the gray axis is its chroma (C_{ab}^*), how vivid it is, and its angle around the axis is its hue angle (h_{ab}), measured in degrees from the red direction. The coordinates come from the CIE's three standard numbers by a fixed formula built on the opponent channels: the green-red coordinate is the red-green signal and the blue-yellow coordinate the yellow-blue one.

Looking straight down the lightness axis, as in Figure 6(a), shows where all 78 Golden paints fall on the plane of the two color coordinates when they are used straight from the tube. The yellows sit at the top, the reds to the right, the blues at the bottom and the greens to the left, and the farther a paint lies from the center, the more vivid its color. The dark transparent paints, the phthalos, the quinacridones and dioxazine, cluster near the center. Straight from the tube they are nearly black, and a near black has little chroma whatever its hue; their color appears only when they are thinned or mixed with white, as Section 3.4 explains.

(a) the 78 masstones in the a^*b^* plane: chroma is the radius, hue the angle

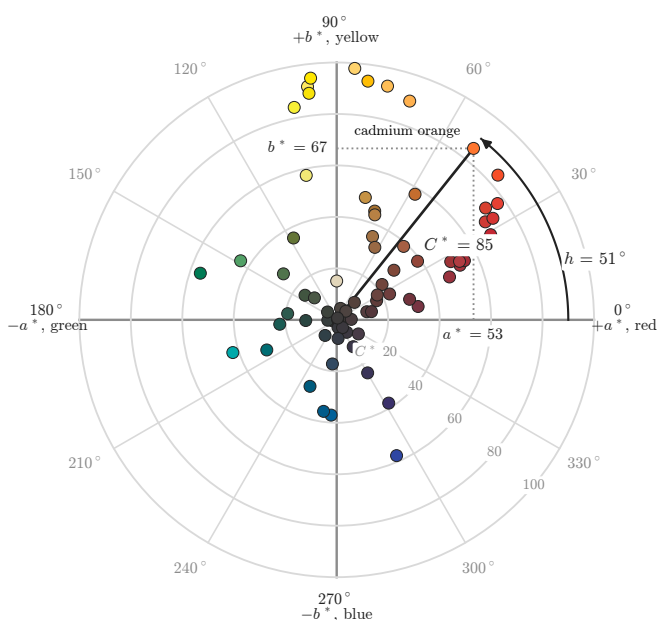
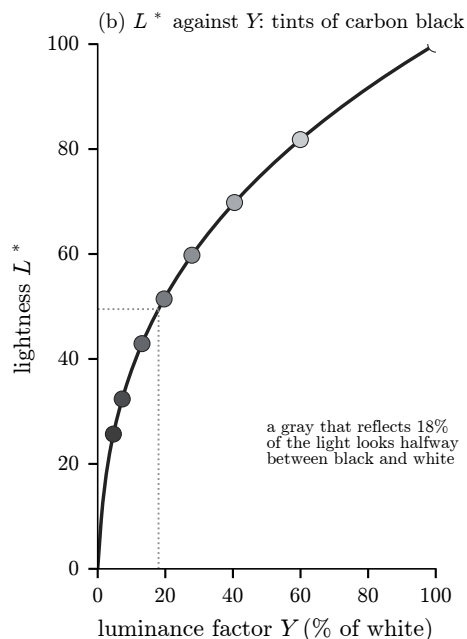


Figure 6: CIELAB. (a) The 78 Golden masstones in daylight, seen from above on the a^*b^* plane, each drawn in its own color; for one paint, cadmium orange, the chroma (the distance from the center) and the hue angle are drawn in. (b) Lightness against the share of the light a surface reflects, with tints of carbon black in titanium white marked on the curve; the tints are computed with the mixing model.

Lightness does not grow in step with the amount of light. Panel (b) shows the relation: a gray that reflects only 18 percent of the light already looks halfway between black and white, and the remaining 82 percent of the light covers the other half of the lightness scale. This compression of value is necessary to accurately represent our visual perception. It means a small change in the

light reflected is a bigger step of value among the darks than among the lights. The painter's rule that a little black goes a long way in a tint comes mainly from the paint itself: near white, the first trace of an absorbing pigment takes away a large share of the light (Section 2.1).

Because CIELAB is built so that equal distances look roughly equally different, the difference between two colors can be measured as the distance between them, and a difference of about one unit is close to the smallest a careful observer can see [3]. The space is not perfectly even: the same distance looks larger among grays than among vivid colors. So this paper uses a refined measure of difference called CIEDE2000, which weights the parts of a difference to match what people see [45, 67]. Its unit is what this paper calls a unit of color difference, written ΔE_{00} in the figures. More even spaces exist, but for paint mixing CIELAB is good enough, and every pigment manufacturer, Golden included, publishes in it. A CIELAB color is always measured against a white under a particular light, and in this paper the light is daylight unless stated otherwise.

One more way of drawing color comes up later: the CIE's chromaticity diagram. It is a flat map of colors with the amount of light taken out, so a color and a darker or lighter version of it land on the same spot. The single wavelengths of the spectrum lie around its curved, horseshoe-shaped edge, violet at one end and red at the other, and white sits near the middle; where a color lies between white and the edge shows its hue and how pure it is. Its most useful property is that a mixture of two lights always lies on the straight line between them, so three lights can make exactly the colors inside the triangle they mark out. Mixtures of paints do not follow straight lines, on this map or any other, as Part 3 shows. The formulas for CIELAB, for color differences and for the chromaticity diagram are in Section 1.9.

1.8. What a gamut is. No set of colorants, lights or inks can make every color. The set of colors a system can make is its gamut, and the gamut of a painter's palette is the set of colors that can be mixed from it. Gamuts are best pictured one lightness at a time: at a given lightness there is an outer boundary beyond which no surface of any kind can go, a smaller region a monitor can show, and a smaller region still that a given set of paints can reach. Real paints fall well inside the physical limit, and the most vivid of them, the cadmium yellows and oranges, fall outside what a monitor can show, so no picture in this paper, on a screen or printed, can show them as vivid as they are.

The regions are drawn at two lightnesses in Figure 7. The outer line is the physical limit. It belongs to ideal surfaces that reflect all of the light in one band of wavelengths and none outside it, or the reverse. These are called the optimal colors, and they are the most vivid surfaces that could exist at that lightness [47]. The dashed line is what an ordinary monitor can show [36]. The inner solid line is what the 26 calibrated paints can reach by mixing them two at a time and adding white, as the model computes it; the dots are those paints and their tints near that lightness. At a lightness of 75 the yellows go beyond what the monitor can show. At 50, the middle of the scale, the reds and violets are well inside the monitor's range while the greens and green-blues go beyond it, and at both levels everything the paints reach is far inside the physical limit.

Real pigments fall short of the physical limit because their absorption does not switch on and off sharply at the edge of a band, and they absorb some of the light they ought to pass. Cadmium yellow medium, the most vivid paint in the Golden set, has a chroma of 98, while the optimal color of the same lightness and hue would have 146. Pointer collected the most vivid real surfaces he could find, of every kind, and his gamut of real surface colors is the usual reference for what

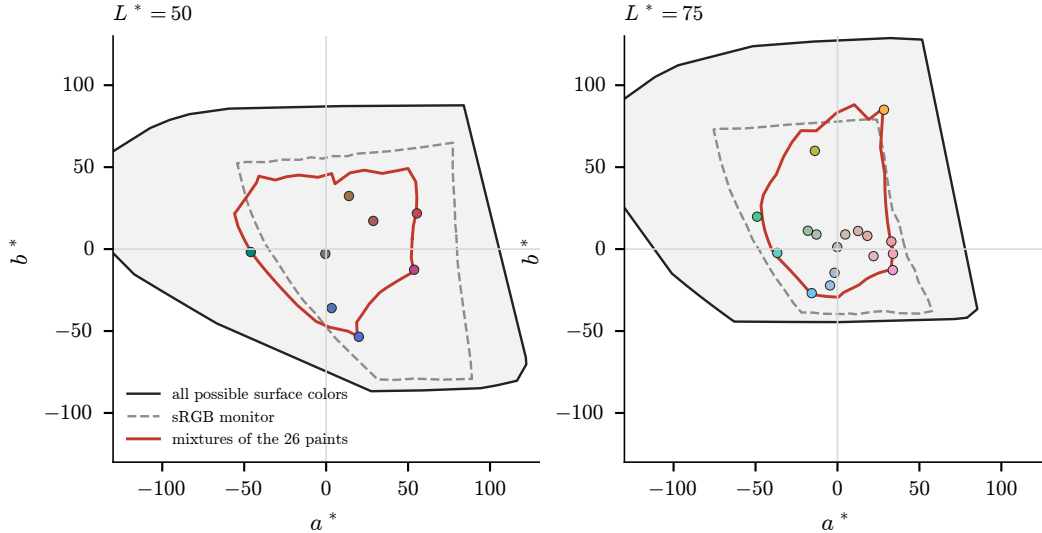


Figure 7: Gamuts at two lightnesses, on the a^*b^* plane. The outer line is the limit of all possible surface colors (MacAdam’s optimal colors [47]). The dashed line is the limit of an ordinary sRGB monitor [36]. The inner solid line is the region reached by mixing two of the 26 calibrated Golden paints at a time with white, computed with the mixing model; the dots are those paints and their tints within three units of the lightness.

paints and dyes have reached [61]; the most vivid modern pigments pass it in a few places.

A monitor’s limit is of a different kind. It makes every color by mixing three fixed lights, and mixtures of three lights can only fill the triangle between them on the chromaticity diagram (Section 1.7). On the color plane of Figure 7, which shows one lightness at a time, the monitor’s range appears instead as the irregular dashed shape. An ordinary monitor misses the most vivid greens, cyans and yellows of real surfaces [36], and twelve of the 78 Golden masstones lie outside its range, among them three of the cadmium yellows, cadmium orange and cobalt teal. Every swatch in this paper has been brought inside the monitor’s range where necessary by reducing its chroma while keeping its lightness and hue, so the pictures understate the chroma of the most vivid paints and never their lightness or their hue.

1.9. Appendix: the mathematics.

Light, illuminants and reflectance (Section 1.1). Light is electromagnetic radiation, and its wavelength λ is the distance between successive crests. The eye responds from about 380 to 780 nm, with almost all of its sensitivity between 400 and 700 nm [78]. A light source is described by its spectral power distribution $E(\lambda)$, the power it emits at each wavelength. The CIE’s illuminant D65 is a standard daylight, derived by Judd, MacAdam and Wyszecki from measurements of real daylight, with a correlated color temperature of 6500 K [38]. Illuminant A is the spectrum of a blackbody radiator at 2856 K, close to a tungsten filament. With both scaled to the same output at 560 nm, as in Figure 1(b), daylight is nearly flat and illuminant A gives five to ten times as much light at the red end as at the blue, depending on which wavelengths are compared. Both are tabulated by the CIE [11]. A surface that does not emit light is described by its spectral reflectance factor $R(\lambda)$, the ratio of the light it sends back to the light a perfect white

diffuser would send back under the same illumination and viewing geometry; R lies between 0 and 1 for an ordinary surface. The light that reaches the eye from the surface is the product

$$L(\lambda) = E(\lambda) R(\lambda), \quad (1)$$

the illuminant's spectrum multiplied, wavelength by wavelength, by the surface's reflectance. The eye sees $L(\lambda)$, not $R(\lambda)$.

Measured reflectance factors depend on the geometry of the measurement. The Golden data were taken with an integrating sphere that collects the light reflected in all directions, including the few percent that bounces off the top surface of the paint without entering it [24]. That is why every dark paint in the set bottoms out between 3.7 and 4.8 percent: the floor is the surface reflection of a film of refractive index $n \approx 1.5$, which is $((n - 1)/(n + 1))^2 \approx 4$ percent at normal incidence [30]. Of the curves in Figure 1(c), cadmium yellow medium reflects less than 5 percent below about 490 nm and more than 90 percent above about 580 nm, and phthalo blue reflects 11 percent at its peak near 450 nm and less than 5 percent everywhere above 520 nm.

Cone signals and tristimulus values (Section 1.2). The human retina has about 4.6 million cones and about 92 million rods [17]. The S cones make up about 5 percent of the cones and are absent from the very center of the fovea [17, 18], and the ratio of L to M cones ranges from about 1 to 1 to more than 16 to 1 in one study of observers with normal color vision [33]. The L, M and S sensitivities peak near 570, 545 and 445 nm; the L and M peaks are only about 25 nm apart [70]. Each cone contains a photopigment that absorbs light with a probability depending on wavelength, and the cone's output depends only on the total number of photons absorbed. This is the principle of univariance: a cone cannot tell a few photons at its best wavelength from many photons at a poor one. The signal from a cone of type i exposed to a light $L(\lambda)$ is therefore

$$c_i = \int \bar{c}_i(\lambda) L(\lambda) d\lambda, \quad i = L, M, S, \quad (2)$$

where $\bar{c}_i(\lambda)$ is the cone's spectral sensitivity, and two spectra that give the same three numbers are indistinguishable.

The cone signals are rarely used directly in color work. The CIE's 1931 standard observer, built from the matching experiments of Wright and Guild [77, 27], defines three color matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ that are linear combinations of the cone sensitivities, and the tristimulus values

$$X = k \int \bar{x}(\lambda) E(\lambda) R(\lambda) d\lambda, \quad Y = k \int \bar{y}(\lambda) E(\lambda) R(\lambda) d\lambda, \quad Z = k \int \bar{z}(\lambda) E(\lambda) R(\lambda) d\lambda, \quad (3)$$

with k chosen so that a perfect white has $Y = 1$ (or 100). $\bar{y}$ is the eye's sensitivity to brightness, the luminous efficiency function, so Y is the luminance factor, the fraction of the light the surface sends back as the eye weights it. Because X , Y and Z are, to a good approximation, linear combinations of the cone signals, they carry the same information as L , M and S : two lights match for the standard observer if and only if they have the same XYZ . Every color calculation in these notes starts from equation (3), evaluated as a sum over the wavelengths at which the data are tabulated [11]. In Figure 2(b), cadmium yellow medium gives the L, M and S cones 71, 59 and 6 percent of what a white gives them, phthalo blue in masstone 4, 4 and 9 percent, and chromium oxide 14, 15 and 9.

The opponent channels (Section 1.3). Figure 3(a) draws the luminous efficiency $\bar{y}$ (light against dark), $\bar{x}-\bar{y}$ (red against green) and $\bar{y}-\bar{z}$ (yellow against blue). These are the combinations on which the a^* and b^* axes of CIELAB are built, equation (5). Panel (b) uses the simplest cone-opponent combinations, $(L+M)/2$, $L-M$ and $S-(L+M)/2$, with the cone signals scaled so that a white gives 1, 0 and 0. In the retina the midget ganglion cells carry a signal that is in effect $L-M$, the small bistratified cells carry $S-(L+M)$, and the parasol cells carry $L+M$, the luminance signal [19]. Their weightings are not exactly those of the simplest combinations, and the red-green channel’s positive response to violet light, which makes violet look reddish, comes from an S-cone contribution. The signals pass through the lateral geniculate nucleus to the primary visual cortex and on to areas including V4 [79].

Metamers (Section 1.4). Two stimuli $L_1(\lambda)$ and $L_2(\lambda)$ are metamers for an observer if they give equal cone signals, $\int \bar{c}_i L_1 d\lambda = \int \bar{c}_i L_2 d\lambda$ for $i = L, M, S$, or equivalently equal XYZ . A spectrum sampled at 31 wavelengths has 31 degrees of freedom and a match imposes 3 conditions, so the metamers of any color form a 28-dimensional family, and real reflectances provide plenty of them. Grassmann’s laws state that matching is linear: if two lights match, they still match when the same third light is added to both, or when both are scaled by the same factor [26]. That is what equation (2) expresses, and it is the foundation of colorimetry [78]. The metamerism index of a pair is the color difference between them under a test illuminant, given that they match under a reference one [11].

In Figure 4 the mixture is 40 percent hansa yellow medium, 46 percent ultramarine blue and 14 percent titanium white by weight, chosen so that its tristimulus values under D65 come as close to the target’s as three paints allow; with only two free proportions an exact match is not generally possible. The two colors differ by $\Delta E_{00} = 0.9$ under D65, 1.1 under illuminant A and 4.9 under F11. The curves cross four times, near 400 to 410, 520 to 530, 560 to 570 and 620 to 630 nm, and lie almost on top of each other from 430 to 480 nm. Observer metamerism comes from differences in the cone sensitivities with age, with the density of the yellow pigment of the lens and macula, and with the genetics of the L and M photopigments [20].

Adaptation (Section 1.5). In von Kries adaptation [73] each cone class adjusts its gain independently, in inverse proportion to its average excitation. If the cone signals under the adapting light are (L, M, S) and the white of that light gives (L_w, M_w, S_w) , the adapted signals are

$$L' = L \frac{L_{w,\text{ref}}}{L_w}, \quad M' = M \frac{M_{w,\text{ref}}}{M_w}, \quad S' = S \frac{S_{w,\text{ref}}}{S_w}, \quad (4)$$

where the reference white is the one the colors are to be judged against, usually daylight. In practice the transform is applied to a “sharpened” set of three channels, obtained from XYZ by a fixed matrix, in place of the physiological cone signals, because sharpened channels predict the experimental data better; the CAT02 transform of the CIECAM02 model [53] and its successor CAT16 [44] are the standard choices, and CAT02 is what Figure 5 uses. A complete von Kries adaptation would make every surface perfectly color constant only if a change of illuminant were a pure scaling of the cone signals. It is not, because a change of illuminant changes the product $E(\lambda)R(\lambda)$ in a way that depends on the shape of R , which is why the residuals in the figure differ from paint to paint: within $\Delta E_{00} = 1.6$ for titanium white and yellow ochre, 2.9 for ultramarine, 4.0 for phthalo green, 4.4 for quinacridone magenta and 5.1 for pyrrole red. Observers typically adapt about 80 to 90 percent of the way to a colored illuminant [23].

The six attributes (Section 1.6). The CIE’s own definitions are in its vocabulary document [13], and Fairchild’s book sets them out with the experiments behind them [23]. *Brightness* is the attribute of a visual perception according to which an area appears to emit more or less light. *Lightness or Value* is the brightness of an area judged relative to the brightness of a similarly illuminated area that appears white. *Colorfulness* is the attribute according to which the perceived color of an area appears to be more or less chromatic. *Chroma* is the colorfulness of an area judged as a proportion of the brightness of a similarly illuminated area that appears white. *Saturation* is the colorfulness of an area judged in proportion to its own brightness. *Hue* is the attribute according to which an area appears similar to one of the perceived colors red, yellow, green and blue, or to a combination of two of them. So there are two absolute attributes, brightness and colorfulness, and their relative versions, value and chroma, each obtained by dividing by the white; saturation, which is colorfulness divided by the color’s own brightness, or equivalently chroma divided by lightness; and hue.

CIELAB, color differences and chromaticity (Section 1.7). CIELAB was adopted by the CIE in 1976 [11, 62]. From the tristimulus values of a color, X , Y , Z , and those of the reference white, X_n , Y_n , Z_n , define

$$L^* = 116 f\left(\frac{Y}{Y_n}\right) - 16, \quad a^* = 500 \left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right) \right], \quad b^* = 200 \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right) \right], \quad (5)$$

where $f(t) = t^{1/3}$ for $t > (6/29)^3$ and a straight line of matching slope below that, so that the formula behaves well near black. The cube root is the compression of Figure 6(b): a gray with $Y = 0.18$ has $L^* = 49.5$. It descends from the Munsell value scale, which was fitted to judgments of equal lightness steps [58], and it is a fair approximation to the eye’s response over the range of ordinary surfaces. The chroma and hue angle are the polar coordinates of (a^*, b^*) ,

$$C_{ab}^* = \sqrt{a^{*2} + b^{*2}}, \quad h_{ab} = \arctan(b^*/a^*), \quad (6)$$

with the angle taken in the right quadrant so that it runs from 0° to 360° . In Figure 6(a), cadmium yellow medium sits at $b^* = 98$ with a chroma of 98, pyrrole red at a chroma of 68, and cobalt blue at $b^* = -53$. The hue angles of the paints used most in Part 3 are hansa yellow medium 83° , diarylide yellow 72° , pyrrole red 29° , quinacridone magenta 9° , ultramarine blue 302° , cobalt blue 294° , phthalo blue (green shade) 300° , phthalo green (blue shade) 233° , permanent green light 161° and chromium oxide green 139° .

The a^* axis compares X with Y and the b^* axis compares Y with Z ; since $\bar{x}$ is a red-heavy combination of the cones and $\bar{z}$ is almost the S-cone sensitivity, these are the opponent channels of Figure 3 in all but detail. The space is defined relative to a white, so the same surface has different coordinates under different illuminants. This paper uses daylight D65 and the 1931 2° observer unless stated otherwise, which puts its values within a few units of Golden’s own, published for the 10° observer [25].

The simplest measure of color difference, ΔE_{ab}^* , is the Euclidean distance $\sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$, and a difference of about 1 is near the threshold of visibility under good conditions [3]. The space is not quite uniform: equal distances look larger in the neutrals than in saturated colors and larger in some hues than others, as MacAdam’s ellipses had already shown in the chromaticity diagram [46]. The CIEDE2000 formula, whose differences are written ΔE_{00} and are the units of color difference of the main text, corrects for this with weighting functions for lightness, chroma

and hue and a term for the blue region [45, 67]; for small differences it is roughly comparable to ΔE_{ab}^* in the neutrals and smaller than it in saturated colors. Spaces with better uniformity include CAM16-UCS [44] and OKLab [60], and no Euclidean space can be exactly right, since perceived differences do not add along a path the way distances do [7].

The chromaticity of a color is its XYZ with the brightness divided out, $x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$. By Grassmann’s laws, mixtures of lights lie on straight lines in the (x, y) plane. The single wavelengths trace its curved edge, and the straight line joining the two ends of that edge holds the purples.

Gamuts (Section 1.8). Among all reflectances with a given luminance factor, the one with the largest chroma in a given hue direction is a step function, 1 inside a band of wavelengths and 0 outside, or the reverse, with the band chosen to collect the wavelengths that pull the color in that direction and reject the rest. This is MacAdam’s theorem of 1935, and the colors so defined are the optimal colors [47]; they are the outer line of Figure 7. Cadmium yellow medium has a chroma of 98 at $L^* = 86$, and the optimal color of the same lightness and hue has 146. A monitor mixes three fixed lights, and by Grassmann’s laws the mixtures fill the triangle between them in the chromaticity diagram and nothing outside it. Twelve of the 78 Golden masstones lie outside the sRGB triangle [36]: three of the cadmium yellows and the cadmium orange, bismuth vanadate yellow, diarylide yellow and hansa yellow medium, cobalt teal and cobalt turquoise, cerulean blue deep, manganese blue hue and permanent green light. The inner region of Figure 7 mixes every pair of the 26 calibrated paints in steps and brings each mixture to the lightness with white; the boundary follows the outermost of those mixtures. At $L^* = 75$ the yellows pass the monitor’s limit and the reds and oranges come within two to eight units of it; at $L^* = 50$ the greens and green-blues pass it.

2 How paints and surfaces create color

A paint is a layer of pigment particles in a mostly clear binder, sitting on a ground. The binder is the glue that holds the particles and dries to a film, acrylic in every paint measured here, and the ground, or substrate, is whatever the paint is on, such as primed canvas, board or paper. Part 1 treated a surface as a reflectance curve and asked what the eye does with it. This part asks where the curve comes from, starting with what happens to light inside the layer and ending with the pigments themselves. Its last subsection sets out the model used for every mixture in the rest of the paper and how far it can be trusted.

2.1. Reflection, absorption and scattering. Light comes in tiny packets called photons, and a photon that reaches a layer of paint can do one of four things. It can bounce off the top surface without entering; this is the gloss and does not change the wavelength of the photon. Otherwise it goes in, where it meets pigment particles. A particle can absorb the photon, scatter the photon, or let the photon pass undisturbed. To scatter a photon is to send it off in a new direction. A photon that is left undisturbed by the pigment eventually reaches the substrate and is either reflected or absorbed by it. Absorption is what gives a pigment its hue: a pigment absorbs some wavelengths far more than others, and the ones it spares are the color it sends back. Scattering is what makes a paint opaque and what sends the colored light back to the eye. A pigment that scatters strongly is opaque; a pigment that scatters weakly is transparent and in a thick layer is dark, because the light that enters it is mostly absorbed before anything sends it

back.

Figure 8(a) sketches the four ways light interacts with paint. The simplest case is a glaze, a thin layer of transparent paint over a white ground, or a watercolor wash on white paper. Nothing in the layer scatters much, so the light goes straight down to the ground and straight back up, and the paint acts as a colored filter. Each slice of the layer takes away the same share of whatever light reaches it, the way each pair of sunglasses in a stack dims what comes through by the same proportion. So the reflectance, the share of the light that comes back at a given wavelength, falls steeply with the first bit of pigment and more and more gently after that, as panel (b) shows. This is the Beer–Lambert law.

At the other extreme is a layer thick enough that the ground no longer matters, the masstone of Section 1.1. Inside it the light zigzags from particle to particle, losing some to absorption at every step, and the share that finds its way back out depends on a single number: how strongly the paint absorbs divided by how strongly it scatters. Color scientists write this ratio K/S , with K for absorption and S for scattering, after the theory Kubelka and Munk published in 1931 [40]. A paint that absorbs twice as much and scatters twice as much reflects exactly the same, because its light is turned around twice as often, so each leg of its zigzag is half as long, and on each leg it loses the same share as before.

The curve in panel (c) turns K/S into reflectance, and it has a shape every painter knows from the palette. It leaves white nearly vertically: near white, the first trace of an absorbing pigment removes a large share of the light, and each later addition removes much less. It approaches black slowly, so once a mixture is dark, more black changes it little. The dots on the curve are tints of carbon black in titanium white. The first tenth of a percent of black dims the light inside the paint by about a tenth, while going from half black to pure black takes it only from 9 percent to 3. This steep start is the painter’s rule that a little black goes a long way in a tint. Here the reflectance inside the paint means what the paint sends back before the surface reflection is added, the subject of the next subsection.

A particle scatters light because light bends, and partly reflects, wherever it crosses from one material into another, here from the binder into the pigment and out again. How much a material slows light is called its refractive index, and the bigger the mismatch between pigment and binder, the more sharply the light is turned. Scattering is mostly a function of the refractive index of the pigment relative to the binder and the particle size of the pigment. As for size, a given amount of pigment scatters most when its particles are a little under half the wavelength of the light inside the binder, and less when they are much smaller or much larger [50, 4]. Titanium dioxide is made at that size and has a refractive index of 2.7 against the binder’s 1.5, and no other white scatters as much [8]. A phthalocyanine has particles a third or less of the best size, and it absorbs so strongly that what little scattering its particles do is swamped [31]; it colors the binder much as a dye would.

A pigment brings two properties to a paint at every wavelength, how much it absorbs and how much it scatters, and both grow in proportion to the amount of pigment. Its hue comes from the pattern of its absorption across the spectrum: a yellow pigment absorbs the blue and violet and little else, a blue pigment absorbs the red and yellow. Its opacity comes from its scattering. A masstone shows only the ratio of the two, so a masstone alone cannot say how a paint will mix. The appendix to this part (Section 2.7) gives both laws and where they come from.

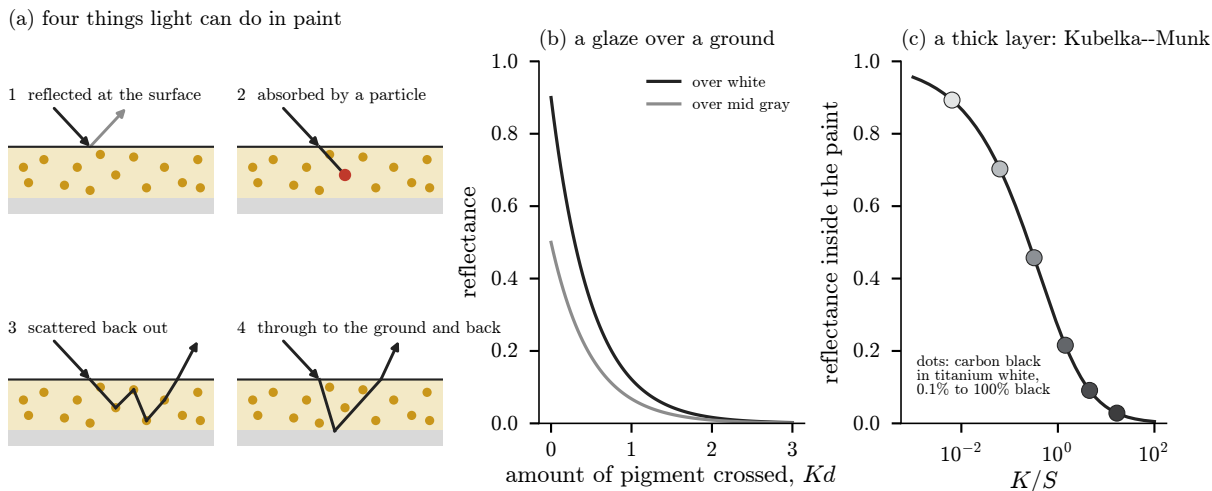


Figure 8: (a) The four things light can do in a layer of paint: reflect off the surface, be absorbed by a particle, be scattered back out, or pass through to the ground and back. (b) A glaze over a white ground and over a gray one. The horizontal axis is the amount of pigment the light crosses, its absorption times the thickness of the layer; the light comes back weaker the more pigment it crosses, falling fast at first and then slowly. (c) A thick layer: the light that comes back depends only on the paint's absorption divided by its scattering, K/S . The horizontal scale is logarithmic: each labeled mark is ten times the one before. The dots are tints of carbon black in titanium white, from 0.1 percent black to pure black, at 550 nm, computed with the model.

2.2. The surface. About four percent of the light never gets into the paint. It is the gloss, reflected off the surface of the binder in every paint and at every wavelength, and the rest of this paper calls it the surface reflection. On a glossy paint it goes off in one direction as a highlight, and from any other direction the paint shows its own color undiluted. On a matte paint the surface is rough and the surface reflection is spread in all directions, so some of it reaches the eye from every angle and mixes a little white light into the color. Matte paint therefore looks paler and duller than the same paint under gloss varnish, and the difference is largest for the darkest colors. There is a second, less obvious effect inside. Light trying to leave the paint meets the same surface from below, and about sixty percent of it is turned back in, to be absorbed or scattered again, mostly because light that meets the surface at a slant from inside cannot get out at all. Both effects are in every measurement of a paint and have to be allowed for before the paint's own absorption and scattering can be worked out.

Golden acrylics measured at the Rochester Institute of Technology (RIT), each one bare and under Golden's matte and gloss varnishes, show the effect of the surface plainly in Figure 9(a); the instrument was placed where the glossy highlight cannot reach it [71]. On the lightness scale, which runs from 0 for black to 100 for white, bone black measures 13 bare, 6 under the gloss varnish and 20 under the matte. The gloss varnish sends the surface reflection off in one direction, away from the viewer, and the black looks blacker; the matte varnish spreads it everywhere and the same black looks gray.

The surface also sets a floor under any measurement that collects the surface reflection. The instrument behind the Golden data collects all of the reflected light, highlight included, so no

(a) measured: the same paint under three surfaces

	unvarnished	matte varnish	gloss varnish
bone black	$\begin{matrix} L^* & 13 \\ C^* & 0 \end{matrix}$	$\begin{matrix} L^* & 20 \\ C^* & 1 \end{matrix}$	$\begin{matrix} L^* & 6 \\ C^* & 0 \end{matrix}$
red oxide	$\begin{matrix} L^* & 33 \\ C^* & 46 \end{matrix}$	$\begin{matrix} L^* & 36 \\ C^* & 39 \end{matrix}$	$\begin{matrix} L^* & 32 \\ C^* & 49 \end{matrix}$
chromium oxide	$\begin{matrix} L^* & 41 \\ C^* & 32 \end{matrix}$	$\begin{matrix} L^* & 44 \\ C^* & 29 \end{matrix}$	$\begin{matrix} L^* & 40 \\ C^* & 34 \end{matrix}$

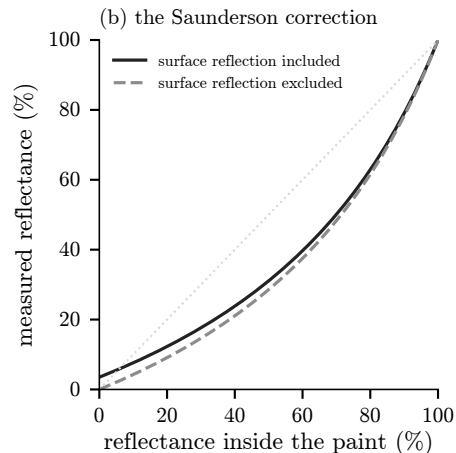


Figure 9: (a) Three Golden acrylics measured bare and under a matte and a gloss varnish, from the RIT Art-SI library [71], with the lightness L^* and chroma C_{ab}^* of each swatch. The matte varnish makes every paint lighter and grayer; the gloss makes it darker and richer. (b) What an instrument reads against what the paint sends back from inside, with the surface reflection included (solid) or left out (dashed). The dotted diagonal would be a paint with no surface. The solid line never reaches zero: the surface sets a floor.

paint can measure below about 3.5 percent there, however black it is, and the darkest paints read about 4. Near that floor a measurement is mostly surface and very little paint, so a near black and a true black read almost the same. Every dark transparent paint in the Golden data sits on this floor over most of the spectrum (Section 2.4), and that is the main reason a masstone measurement of such a paint says so little about it.

Taking the surface back off a measurement is a matter of bookkeeping, which Saunderson worked out in 1942: subtract the light reflected at the top, then allow for the light inside that the surface turns back for another try [64]. Run backward, his formula takes what the instrument reads and gives the reflectance inside the paint, which is what the two laws above describe; Figure 9(b) draws it. The correction is an approximation that works for thick, opaque layers, and it is what the paint industry uses [39, 3]. Section 2.7 has the formula and the optics behind the four and the sixty percent.

2.3. Beyond two fluxes. The Kubelka–Munk law keeps its bookkeeping simple by following only two fluxes of light, a flux here being just the light flowing one way: one runs down through the paint and the other comes back up. It also treats each flux as perfectly diffuse, its light spread evenly over every direction, and Saunderson’s correction assumes the same of the light that meets the surface from inside. In real paint some directions carry more light than others, and the surface lets light out when it meets it nearly head on but turns it back in when it meets it at a slant. The full description, called radiative transfer, follows the light direction by direction instead of lumping it into up and down [9].

In a tint the simple picture is close to the truth, because the white scatters the light so often that it really is spread close to evenly, and the model built on it reproduces measured tints closely (Section 2.6). In a glaze it is not, because nothing in the film scatters to even the light out. Light that crosses the film steeply passes through less pigment than light that crosses at a slant, and in

the colors the pigment absorbs, the short, steep paths let through more light than the simple law allows for. Followed direction by direction, a glaze of the same lightness comes out a few units of chroma less vivid than the simple law makes it, and still far more vivid than a tint of the same lightness. For ease of computation the rest of the paper keeps the simple law, and the error is small: inside the model’s accuracy for tints, and a few units of chroma for glazes, so the glazes of Section 3.6 slightly overstate their chroma. The appendix works through the calculation for four paints.

2.4. Transparent and opaque pigments. A paint is opaque if a thin layer of it hides what is under it, and transparent if the ground shows through, and scattering decides which. Light entering an opaque paint is turned around within a short distance by the pigment particles and comes back out before it ever reaches the ground; light entering a transparent paint goes through to the ground, is reflected there, and comes back through the paint, so what you see is the ground seen through a colored filter. Opaque pigments are usually inorganic, minerals and metal compounds whose particles have a high refractive index and are near the size that scatters best: the cadmiums, the iron oxides, chromium oxide, titanium white. Transparent pigments are usually organic, carbon-based molecules in tiny particles: the phthalocyanines, the quinacridones, dioxazine. In masstone an opaque pigment shows its color fully, since its particles send light back in their own hue, and a dark transparent one is a near black, since almost nothing sends the light back. With white added, the transparent pigment’s color appears, often far more vivid than its masstone suggests.

Golden rates each of its paints on a scale from transparent to opaque, judging by eye a thin layer drawn down over a black and white chart [25]. Figure 10(a) sets that rating beside how strongly each paint scatters green light, gram for gram, compared with titanium white. The model works that number out from Okumura’s tint ladders, the series of each paint mixed with more and more white that he measured (Section 2.6) [59]. The two agree in broad outline. Titan buff, a white tinted with a little oxide, scatters about as much as the white, carbon black, diarylide yellow and naphthol red a quarter to a third as much, and the phthalocyanines about a hundredth. Within each rating the spread is wide. The model’s number is per gram of paint, so it depends on how much pigment the maker put in the tube as well as on the pigment, and Golden’s rating judges a thin film by eye while the model’s number comes from thick ones.

Adding white separates the two kinds. Pyrrole red, rated semi-opaque, is at its most vivid straight from the tube, and every addition of white makes it paler and duller (Figure 10(b)). Quinacridone magenta, rated transparent, starts dark and dull, grows more vivid with white up to a peak near one part white to two of paint, and only then fades. Burnt sienna, which Golden rates opaque but which scatters only a twentieth as much as the white, does a little of both. Section 3.4 explains the peak. The masstone curves in panel (c) show why. Pyrrole red’s particles scatter red light back out, and it reflects most of the red. Quinacridone magenta reflects no more than 61 percent even at the far red end, and across the green and most of the blue it sits on the surface floor, because the light there is absorbed before anything can send it back.

How well a layer hides depends on how far light gets into it before it is turned around. Once the layer is several times that distance thick, very little light reaches the ground and returns, and the ground is hidden. In titanium white the distance is a few thousandths of a millimeter, and a film a few hundredths of a millimeter thick hides [43]. In a phthalocyanine, light goes so far that a film would have to be absurdly thick to hide by scattering alone. It hides in masstone by absorbing nearly everything instead, so its masstone is near black [43]. The trade’s name

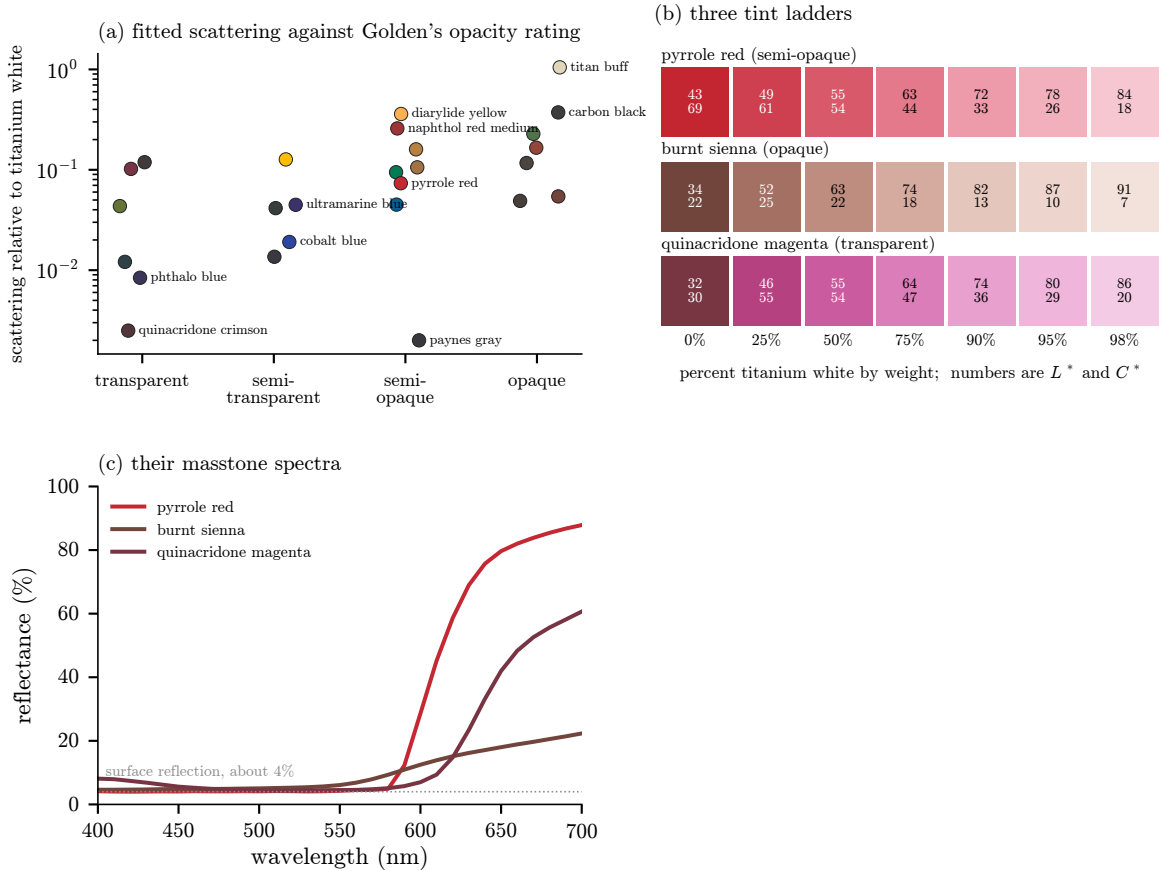


Figure 10: (a) How strongly each calibrated paint scatters green light, gram for gram, compared with titanium white, as the model works it out from measured tints, against Golden's opacity rating [25]. The vertical scale is logarithmic: each labeled mark is ten times the one before. (b) Three paints of different opacity mixed with more and more white, computed with the model; the numbers on each swatch are its lightness L^* and chroma C_{ab}^* . Pyrrole red only fades, while quinacridone magenta first gains color. (c) The measured masstone spectra of the three. The thin line near the bottom is the surface floor.

for a paint's ability to cover is *hiding power*, and absorption adds to it as well as scattering. A transparent paint hides well in the colors it absorbs and poorly in the colors it passes, so a glaze of phthalo blue over white hides the white in the red and shows it in the blue.

Scattering also depends on the binder and on how much of it there is. The same pigment scatters more in air than in oil or acrylic, because the mismatch of refractive index is larger: a dry pastel or an underbound, chalky paint is lighter and more opaque than the same pigment well bound, and a wetted pastel darkens as the liquid fills the air spaces [72]. When a paint has so much pigment that the binder can no longer fill the spaces between the particles, a point called the critical pigment volume concentration, air pockets appear in the film and scatter on their own, and the paint turns matte and opaque at once [2, 66]. The Golden Heavy Body paints are well short of that point, and the measurements here are of fully bound films.

A paint does not scatter the same amount at every wavelength, and that matters for mixing.

White pigments scatter most at the blue end, which Section 3.7 takes up. Colored pigments tend to scatter most just past the long-wavelength edge of the colors they absorb, on the side toward the red, because a material's refractive index changes fastest near the wavelengths it absorbs [43, 39]. Okumura saw the scattering change across the spectrum in his tint ladders of the Golden paints, most clearly for phthalo green [59]. The model lets each paint's scattering vary across the spectrum, and without that it cannot reproduce the measured tints of the phthalocyanines.

2.5. Pigment types, with examples. Pigments get their colors in a few different ways, and the way decides the shape of the reflectance curve. The cadmiums are semiconductors, crystals whose absorption switches on sharply at one wavelength: they absorb every wavelength shorter than a cutoff and reflect everything longer, so their curves are a single step, placed at a different wavelength for yellow, orange and red. The iron oxide earths, the cobalts and chromium oxide owe their colors to metal ions, charged atoms of iron, cobalt or chromium held in a crystal; their absorptions are broad and their curves are rounded, so they are duller than the cadmiums. The organic pigments, the phthalocyanines, quinacridones, azo yellows, pyrroles and dioxazine, are colored molecules; their absorptions are strong and often fall in bands with clear edges, and they are transparent because their particles are small and absorb so strongly that their scattering hardly shows. Blacks absorb everything and whites absorb nothing. Figure 11 groups the curves of 55 of the 78 Golden paints this way.

Each family has a look of its own. The cadmiums are the cleanest curves in the set, each a single step from almost nothing to almost everything; cadmium yellow light makes its whole climb between 480 and 540 nm. The iron oxides rise gently from the blue to the red and never reflect more than half the light, and the umbers stay low everywhere. The cobalt and chromium pigments have humped curves with two or three bands, and cobalt blue, besides its blue band, rises again at the far red end, where most eyes barely see. Ultramarine reflects a narrow band of blue and nothing else. Of the organic pigments, the phthalocyanines lie flat near the floor with a small bump in the blue or blue-green, the quinacridones rise steeply to a red plateau, the azo yellows are steps like the cadmiums but a little lower, and dioxazine and anthraquinone blue are flat and near black. The paints Golden labels as hues are mixtures of several pigments made to imitate a historical color, and their curves combine those of their ingredients.

The cadmium step comes from the crystal as a whole. A semiconductor absorbs every photon carrying more than a certain energy and none carrying less, and since blue and violet light carry more energy than red, a cadmium absorbs everything on the blue side of a cutoff and reflects everything on the red side. In cadmium sulfide the cutoff falls in the green, so it absorbs the violet, blue and green and is yellow; replacing some of the sulfur with selenium moves the cutoff through orange to red [57]. Because the cutoff belongs to the whole crystal rather than to single atoms, it is sharp, and that sharpness gives the cadmiums the highest chroma of any opaque pigment.

The earths are colored by iron, which absorbs the short wavelengths heavily and the long ones partly and so gives them their gently rising curves [68]. Yellow ochre and raw sienna owe their color to goethite, an iron oxide with water bound into it; red oxide and burnt sienna owe theirs to hematite, which has none, and heating goethite turns it into hematite, which is what "burnt" means. The umbers contain manganese as well as iron and absorb across the whole spectrum. In the cobalt pigments and chromium oxide the metal ions sit in a crystal that sets where they absorb: cobalt blue absorbs the orange and red and passes the blue, cerulean and cobalt teal are

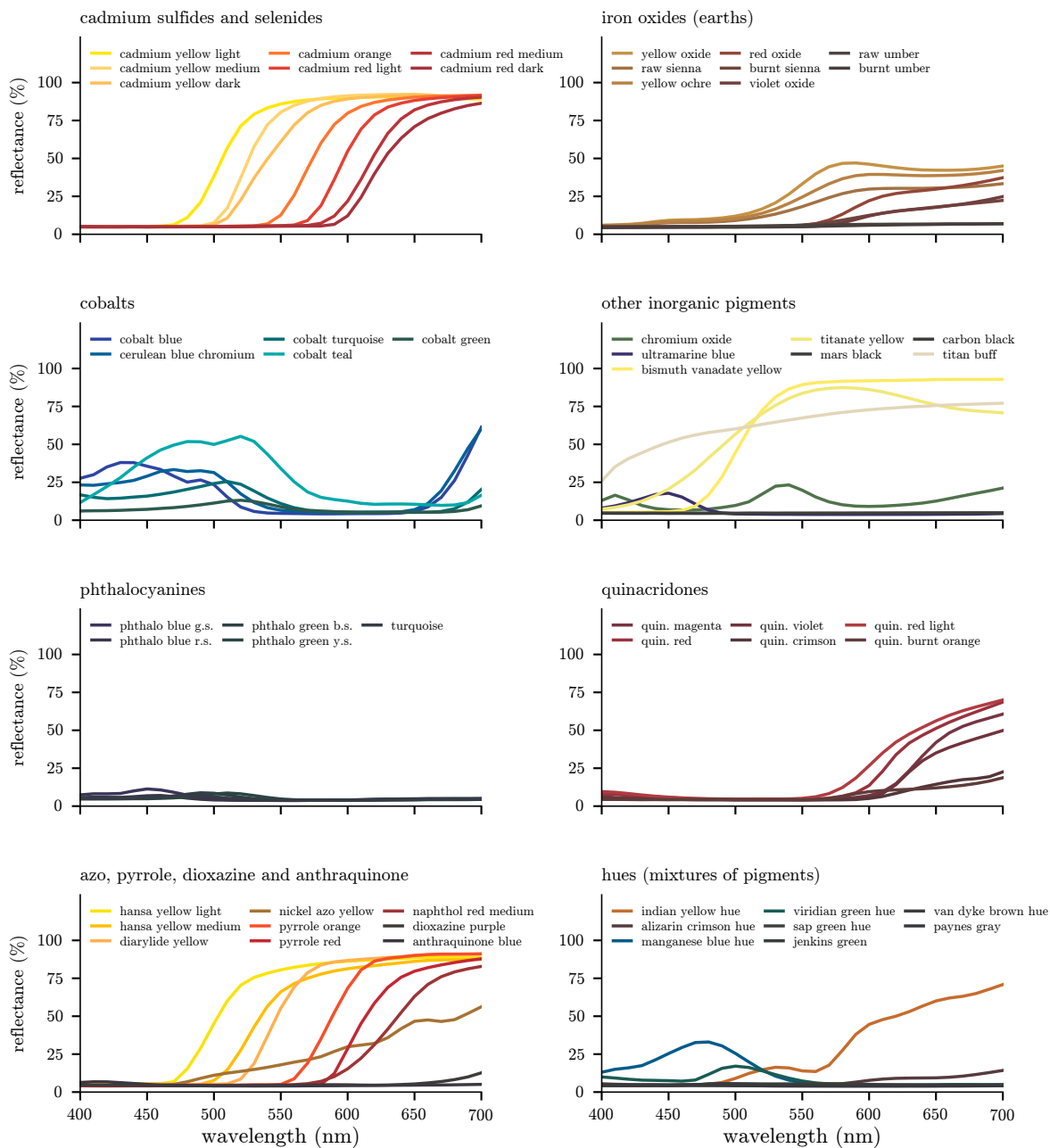


Figure 11: The measured masstone reflectance of the Golden Heavy Body paints [24], grouped by the kind of pigment, each curve drawn in the paint's own color. The cadmiums are clean steps, the earths rise gently, the cobalts have humps, and the dark organic pigments lie along the floor.

cobalt in other crystals with the bands shifted, and chromium oxide absorbs the violet and the red and passes a band of green [57]. Ultramarine’s color comes from small clusters of three sulfur atoms trapped in a cage of sodium aluminum silicate, which absorb a broad band centered in the orange and pass the blue, and since its refractive index is about the binder’s, its particles barely scatter and it is transparent [8].

The organic pigments are molecules whose electrons absorb visible light. The color comes from the extent of a network of alternating chemical bonds along which those electrons can move, and the pigment is a solid because the molecules pack into tiny crystals that do not dissolve in the binder. Phthalo blue absorbs strongly from the yellow-green through the red and weakly in the blue, and the phthalo greens are its relatives with chlorine and bromine added. The quinacridones absorb from the violet to the orange and pass the red and some violet, which puts them on the magenta side of red. The hansa and diarylide yellows absorb the blue with an edge like the cadmiums’ but less sharp. Pyrrole red has its edge in the orange and, with larger particles than the others, is nearly as opaque as a cadmium. Dioxazine absorbs almost everything and passes a trace of violet and red, so it is nearly black in masstone and a vivid violet in tints [57, 25]. The particles of these pigments are a third or less of the size that scatters best, and in the colors they absorb, their absorption is so strong that the little scattering they do is hard to see [31].

Carbon black absorbs nearly everything across the spectrum; mars black, an iron oxide, absorbs less evenly and scatters more, which makes it the more opaque black and the warmer one in tints. Titanium dioxide absorbs nothing in the visible, apart from a trace at the violet end where its absorption of ultraviolet light spills over, and scatters more than any other white [8]; Section 3.7 shows what that and the scattering do in mixtures. Section 2.7 adds the chemistry behind these curves. Table 1 lists all 78 paints with their pigments, opacity ratings and measured colors.

Table 1: The 78 Golden Heavy Body paints in the spectral data, in order of hue. Pigments and opacity ratings are from Golden’s pigment chart [25]; the seven marked with a star are no longer in the chart and their pigments are from Golden’s earlier listings. The 26 paints marked with a dagger have tint ladders measured by Okumura and are the only ones the model mixes (Section 2.6); the other 52 appear in this paper only as measured masstones. L^* , C_{ab}^* and h_{ab} are computed from the measured masstone spectra under D65 for the 2° observer.

paint	pigment	kind	opacity	L^*	C_{ab}^*	h_{ab}
Permanent Maroon	PR122, PY150, PR101, PG7	mixture	transparent	27	6	2
Quinacridone Magenta [†]	PR122	organic	transparent	31	32	9
Quinacridone Crimson [†]	PR206*	organic	transparent	26	14	13
Alizarin Crimson Hue	PR122, PY150, PG7	mixture	transparent	28	12	15
Quinacridone Violet	PV19	organic	transparent	30	29	16
Quinacridone Red	PV19	organic	transparent	37	47	21
Mars Black	PBk11	inorganic	opaque	26	0	21
Cadmium Red Dark	PR108	inorganic	opaque	39	52	24
Pyrrole Red Dark	PR264	organic	semi-opaque	38	55	25
Quinacridone Red Light	PR207*	organic	transparent	43	53	25
Quinacridone Burnt Orange	PO48*	organic	transparent	29	17	26
Violet Oxide	PR101	inorganic	opaque	33	23	26
Naphthol Red Medium [†]	PR5	organic	semi-opaque	38	50	27
Cadmium Red Medium	PR108	inorganic	opaque	43	62	28
Pyrrole Red [†]	PR254	organic	semi-opaque	43	68	29
Dioxazine Purple [†]	PV23	organic	transparent	25	2	30

paint	pigment	kind	opacity	L^*	C_{ab}^*	h_{ab}
Transparent Red Iron Oxide	PR101	inorganic	transparent	33	18	31
Pyrrole Red Light	PR255	organic	semi-opaque	48	72	33
Naphthol Red Light	PR112	organic	semi-transparent	48	69	33
Cadmium Red Light	PR108	inorganic	opaque	53	77	36
Red Oxide [†]	PR101	inorganic	opaque	39	39	36
Transparent Pyrrole Orange	PO71*	organic	transparent	50	72	37
Burnt Sienna [†]	PBr7	inorganic	opaque	34	22	38
Quinacridone Nickel Azo	PY150, PO48	mixture	transparent	37	29	41
Pyrrole Orange	PO73	organic	semi-opaque	57	84	42
Transparent Brown Iron Oxide	PR101, PBk7	mixture	transparent	29	5	43
Burnt Umber Light	PBr7	inorganic	semi-opaque	29	10	45
Carbon Black [†]	PBk7	inorganic	opaque	26	0	48
Mars Yellow	PBr6	inorganic	opaque	48	39	48
Burnt Umber [†]	PBr7	inorganic	opaque	28	5	49
Cadmium Orange	PO20	inorganic	opaque	65	85	51
Indian Yellow Hue	PY175, PY150, PR206	mixture	transparent	55	58	58
Transparent Yellow Iron Oxide	PY42	inorganic	transparent	49	32	62
Van Dyke Brown Hue	PR101, PBk7	mixture	semi-opaque	25	1	65
Raw Sienna [†]	PY43	inorganic	semi-opaque	52	35	67
Yellow Ochre [†]	PY43	inorganic	semi-opaque	58	43	70
Nickel Azo Yellow	PY150	organic	transparent	52	45	71
Diarylide Yellow [†]	PY83	organic	semi-opaque	78	90	72
Raw Umber [†]	PBr7	inorganic	opaque	29	5	72
Yellow Oxide	PY42	inorganic	semi-opaque	64	49	77
Cadmium Yellow Dark	PY35	inorganic	opaque	81	93	78
Hansa Yellow Medium [†]	PY73*	organic	semi-transparent	81	94	83
Cadmium Yellow Medium	PY35	inorganic	opaque	86	98	86
Titan Buff [†]	PW6:1, PW6	mixture	opaque	86	15	90
Cadmium Yellow Light	PY35	inorganic	opaque	91	94	96
Hansa Yellow Light	PY3*	organic	transparent	90	89	97
Bismuth Vanadate Yellow	PY184	inorganic	semi-opaque	92	91	97
Cadmium Yellow Primrose	PY35	inorganic	opaque	93	84	101
Titanate Yellow	PY53	inorganic	semi-opaque	91	57	102
Green Gold [†]	PY150, PG36, PY175	mixture	transparent	46	36	118
Terre Verte Hue	PG17, PBr7, PBk9, PY42, PG36	mixture	transparent	36	12	135
Chromium Oxide [†]	PG17	inorganic	opaque	45	27	139
Sap Green Hue	PR101, PY150, PG36, PBk7	mixture	semi-transparent	28	5	139
Chromium Oxide Dark	PG17	inorganic	opaque	34	16	142
Cobalt Titanate Green	PG50*	inorganic	semi-opaque	60	44	148
Permanent Green Light [†]	PY175, PG7, PW6	mixture	semi-opaque	45	56	161
Cobalt Green	PG26	inorganic	semi-opaque	35	19	173
Phthalo Green (yellow shade)	PG36	organic	transparent	27	12	181
Jenkins Green [†]	PBk9, PG36, PY150	mixture	semi-transparent	26	3	182
Viridian Green Hue	PW6, PB15:3, PBr7, PY150	mixture	semi-transparent	35	22	184
Hookers Green Hue	PY150, PB60, PR122	mixture	semi-transparent	26	1	197
Cobalt Teal	PG50	inorganic	semi-opaque	63	42	197
Cobalt Turquoise	PB36	inorganic	semi-opaque	42	30	203
Phthalo Green (blue shade) [†]	PG7	organic	transparent	26	8	233
Cerulean Blue Deep	PB36	inorganic	semi-opaque	36	28	248
Manganese Blue Hue	PW6, PB15:3, PG7	mixture	semi-transparent	37	36	262
Azurite Hue	PBr7, PW6, PB15:0	mixture	semi-transparent	31	17	264
Cerulean Blue Chromium [†]	PB36*	inorganic	semi-opaque	39	37	267
Turquoise	PG7, PB15:3	mixture	transparent	25	7	274
Bone Black	PBk9	inorganic	semi-opaque	24	0	278
Paynes Gray [†]	PB29, PBk7	mixture	semi-opaque	24	3	281

paint	pigment	kind	opacity	L^*	C_{ab}^*	h_{ab}
Cobalt Blue [†]	PB28	inorganic	semi-transparent	33	58	294
Phthalo Blue (green shade) [†]	PB15:3	organic	transparent	24	24	300
Phthalo Blue (red shade)	PB15:0	organic	transparent	24	12	302
Ultramarine Blue [†]	PB29	inorganic	semi-transparent	24	38	302
Prussian Blue Hue	PBk9, PB15:0, PV23	mixture	semi-transparent	24	4	307
Anthraquinone Blue [†]	PB60	organic	semi-transparent	24	6	309
Permanent Violet Dark	PR122, PB60	mixture	transparent	27	10	327

2.6. The model used in this paper. Apart from Okumura’s measured tints, every mixture in the rest of this paper is computed, not measured, and this subsection says how it is done and how far the results can be trusted. The model needs two numbers for each paint at every wavelength, how strongly it absorbs and how strongly it scatters, and it gets them in three steps before it mixes anything.

1. *Read the masstone.* Golden measured 78 of its Heavy Body acrylics in layers thick enough to hide the white card beneath them for all but the most transparent colors, and published the reflectance of each across the visible spectrum [24]. The model takes the surface reflection off with Saunderson’s correction (Section 2.2) and reads the paint’s K/S off the curve of Figure 8(c), one wavelength at a time. That ratio is not enough to mix with: two paints with the same masstone can mix quite differently if one scatters much more than the other, and a masstone cannot say how strongly a paint scatters.
2. *Use a tint ladder.* A tint ladder is a series of mixtures of one paint with more and more white. Every paint’s scattering is measured against the white’s, and in the paler tints the white does most of the scattering, so the tints show how strongly the paint absorbs; set beside the masstone’s ratio, that gives how strongly the paint scatters. Okumura, in Berns’s laboratory at RIT, painted and measured tint ladders for 26 Golden paints, using Golden’s Matte Fluid line, which has the same pigments as the Heavy Body paints [59]. The white in every ladder and every mixture is Golden’s titanium white, measured at the Rochester Institute of Technology [71].
3. *Fit.* Fitting means trying values for the unknown numbers until the model’s tints come out as close as possible to the measured ones. For each of the 26 paints the model tries a scattering strength, lets that scattering rise or fall smoothly across the spectrum, and nudges the absorption in the colors where the masstone sits on the surface floor and says nothing reliable. Five numbers per paint are adjusted this way until the computed ladder comes as close as it can to Okumura’s.

These 26 are the calibrated paints of the rest of the paper, and only they are mixed anywhere in it. The other 52, among them the cadmiums, cerulean blue deep and the cobalt greens, teal and turquoise, have no measured ladder and appear only as measured masstones; Table 1 marks which are which.

With each paint’s absorption and scattering in hand, a mixture is simple. Its absorption is the sum of its paints’ absorptions and its scattering the sum of their scatterings, each in proportion to the amount of paint by weight. This is Duncan’s two-constant form of the Kubelka–Munk law [22], named for the two numbers each paint brings at every wavelength. The mixture’s ratio goes back through the curve to give the reflectance inside the paint, the surface reflection is put

back on top, and the result is what Golden’s instrument would have read. The color follows as in Part 1. The formulas and the fit are written out in Section 2.7.

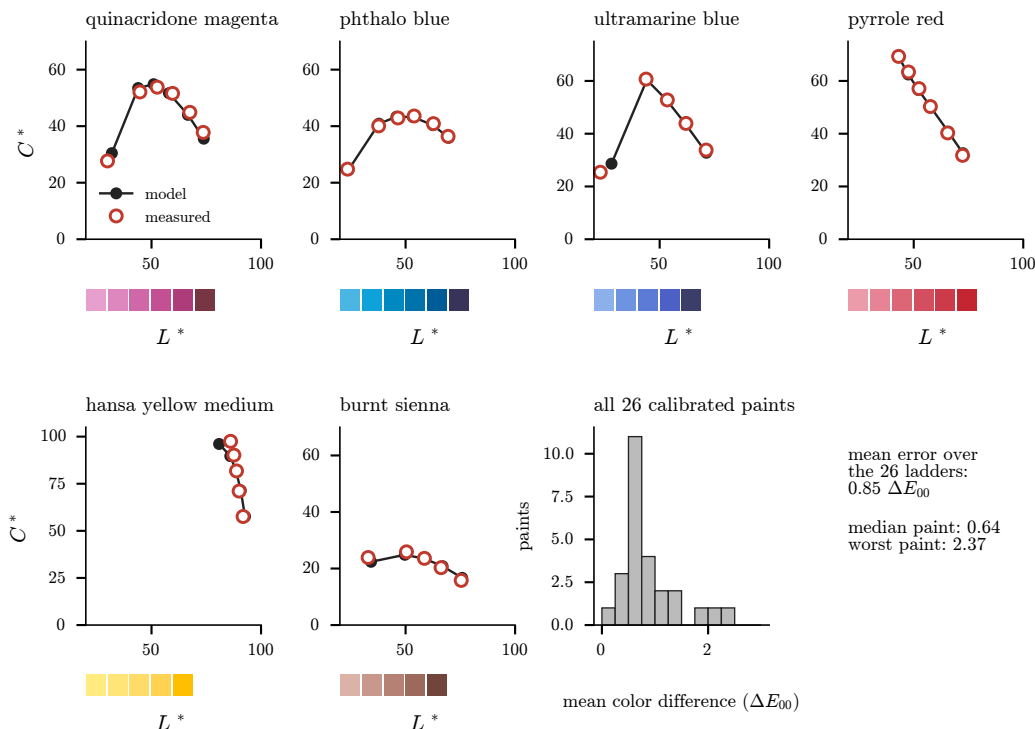


Figure 12: The model against measurement. For six paints, Okumura’s measured tints (open circles) and the model’s prediction for the same recipe (dots), plotted as chroma against lightness, with the model’s colors below [59]. The histogram counts the 26 calibrated paints by the model’s average error over each ladder, in units of color difference, where 1 is about the smallest difference a careful observer can see.

Set beside Okumura’s measurements in Figure 12, the model’s tints land on average within about one unit of color difference of the real ones. The worst paint, hansa yellow medium, is off by about two and a half, for a known reason: the ladder used for it is of Okumura’s Hansa Yellow Opaque, a different product with a lighter masstone. The transparent paints whose color rises and falls as white is added, such as quinacridone magenta and phthalo blue, come out with their peak in the right place and at the right height.

The model has limits too. Mixtures of two colored paints were never measured here, only tints with white. Okumura’s own test of his model on two-paint mixtures found an average error of about two units and eight at worst, for a translucent yellow mixed with ultramarine [59], and this model’s errors for such mixtures are probably of that order. Mixing is by weight of paint, as Okumura’s ladders were, so the proportions are not proportions of pigment, and a strong transparent paint goes much further per gram than a dense opaque one. The masstones of the most transparent paints were measured on films that do not quite hide the white card, so a little of the card shows through in their measurements.

Another weak point of the model is the shape of each paint’s scattering across the spectrum. Nobody measured it: the rise and fall that step 3 allows is whatever made the ladders come

out right, and it is poorly pinned down in the colors a paint absorbs. For the phthalos and pyrrole red it makes the scattering climb steeply toward the deep red. The direction of that rise is real (Section 2.4); its size in the model, many times the white's at the far red end, is not. In green light, by contrast, the phthalos scatter only about a hundredth as much as the white. The shapes should be read as what the ladders needed, and Parts 3 and 4 point back here where a result depends on them. The step-3 adjustments also shift the model's masstones slightly away from the measured ones, for most paints by less than a unit of color difference and for ultramarine by about five, and the masstones quoted in Parts 3 and 4 are the model's. Finally, the Kubelka–Munk law is itself an approximation (Section 2.3). None of this changes which way the effects go, and the figures say where a number is uncertain.

2.7. Appendix: the mathematics.

Absorption, scattering and the two laws (Section 2.1). Mie theory gives the scattering of a sphere of any size and refractive index [50, 4]. Per unit volume of pigment the scattering is greatest when the particle's diameter is a little under half the wavelength inside the binder, which for visible light and a binder of index 1.5 is 0.2 to 0.3 μm . It falls off for particles much smaller, which scatter per unit volume of pigment as the cube of their size, and for particles much larger, whose scattering grows only as their surface. Titanium dioxide is made at the best size and has a refractive index of 2.7 [8]; a phthalocyanine's particles are about 0.1 μm [31].

The Beer–Lambert law describes a film without scattering. If K is the absorption coefficient at some wavelength, the fraction of light absorbed in crossing a thin slice of thickness dz is $K dz$, so the transmittance of a film of thickness d is $T = e^{-Kd}$, and over a ground of reflectance R_g the film reflects

$$R = R_g e^{-2Kd}, \quad (7)$$

the factor 2 because the light crosses the film down and back. K is proportional to the concentration of pigment, so Kd is the amount of pigment the light crosses, and for two pigments in one film the exponents add. The law is exact for light crossing a clear film straight down and straight back; light returning from a diffuse ground crosses at all angles and travels a little further, which in effect thickens the film slightly. It governs glazes, watercolor washes and inks on paper [3].

Kubelka and Munk's law describes a layer that scatters [40]. It follows two fluxes of diffuse light, I going down and J coming up, through a layer with an absorption coefficient K and a scattering coefficient S per unit thickness, both depending on wavelength. In a slice dz the downward flux loses $(K + S)I dz$, part absorbed and part turned around, and gains $SJ dz$ from the upward flux turned around; the upward flux does the same in reverse. For a layer thick enough that the ground does not matter the solution is

$$R_\infty = 1 + \frac{K}{S} - \sqrt{\left(\frac{K}{S}\right)^2 + 2\frac{K}{S}}, \quad \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty}, \quad (8)$$

the second form being the first solved for the ratio. Only the ratio appears. For small K/S the reflectance falls as $1 - \sqrt{2K/S}$, the vertical start of the curve in Figure 8(c), and for large K/S it falls as $S/2K$, the slow tail. The square root belongs to multiple scattering in general and does not depend on the two-flux simplification: in any thick layer that scatters strongly and absorbs weakly, light wanders a long way before it escapes, so the fraction lost grows like the

square root of the absorption [39]. Kubelka’s 1948 solution for a layer of finite thickness over a ground joins the two laws; as the scattering goes to zero it becomes equation (7), and as the thickness grows it becomes equation (8) [3]. For the carbon black tints of Figure 8(c), at 550 nm, the first tenth of a percent of black takes the internal reflectance from 98 to 89 percent, the next nine tenths take it to 70, and going from 50 percent black to 100 percent takes it only from 9 to 3. A pigment contributes $K(\lambda)$ and $S(\lambda)$, each proportional to its amount, and a masstone gives only their ratio, through the second form of equation (8).

The surface (Section 2.2). At the boundary between air and a medium of refractive index n , light at normal incidence is reflected in the fraction $((n - 1)/(n + 1))^2$, which for $n = 1.5$, around where most paint binders sit, is 4 percent [30]; the fraction rises with the angle of incidence and reaches 100 percent at grazing angles. The same boundary seen from inside reflects far more of diffuse light, because every ray beyond the critical angle of 42° is totally reflected; for $n = 1.5$ and perfectly diffuse light the internal reflectance is close to 60 percent [64, 39]. Saunderson wrote the accounting for a paint of internal reflectance R_i in 1942. With k_1 the external reflectance and k_2 the internal one, the light leaving the surface is

$$R_m = k_1 + \frac{(1 - k_1)(1 - k_2) R_i}{1 - k_2 R_i}, \quad (9)$$

the first term being the surface reflection and the second the sum of a geometric series of light that enters, is reflected inside, is turned back by the surface, and tries again [64]. Inverting the formula gives R_i from a measurement, and R_i is what the Kubelka–Munk law describes. Figure 9(b) draws the relation for $k_1 = 0.035$ and $k_2 = 0.6$, the values used for the Golden data in this paper, and with $k_1 = 0$, which is what an instrument that excludes the specular reflection reads. The measured reflectance can never fall below k_1 : an internal reflectance of 1 percent measures 3.9 percent with the surface reflection included, and one of 0.1 percent measures 3.5. The samples of Figure 9(a) were painted on gessoed canvas and board, coated or not with Golden’s matte or gloss MSA varnish, and measured at 45° away from the mirror direction [71]. Bone black has a lightness of 13 bare, 6 under gloss and 20 under matte; red oxide has a chroma of 46 bare, 49 under gloss and 39 under matte. Klein’s criticism is that the formula applies a coefficient for directional light at the top of a model whose light is diffuse everywhere; he has shown that for translucent layers it gives wrong values of K and S , and that models with three or more fluxes do better [39]. For thick, opaque layers the two-flux model with Saunderson’s correction is adequate, and since the same model is used both to extract the coefficients from measurements and to predict mixtures, part of its error cancels [39, 3].

Radiative transfer and the glaze (Section 2.3). The full description is the equation of radiative transfer [9]. In a flat layer of paint, the light at depth z traveling at an angle θ to the downward vertical has an intensity $I(z, \mu)$, where $\mu = \cos \theta$ is positive for light going down and negative for light going up. Along its path a ray loses light to absorption and to scattering out of its direction, and gains light scattered into its direction from every other:

$$\mu \frac{\partial I(z, \mu)}{\partial z} = -(\sigma_a + \sigma_s) I(z, \mu) + \frac{\sigma_s}{2} \int_{-1}^1 p(\mu, \mu') I(z, \mu') d\mu'. \quad (10)$$

Here σ_a and σ_s are the absorption and scattering coefficients of the pigment particles per unit length of path, which follow from Mie theory for particles of a given size and refractive index [4],

and $p(\mu, \mu')$ is the phase function, the share of the light scattered from direction μ' that goes into direction μ , averaged around the vertical and normalized so that $\frac{1}{2} \int_{-1}^1 p d\mu = 1$. The factor μ on the left is the slant: a ray at angle θ crosses a slice of thickness dz along a path of length dz/μ , so a slanted ray meets more pigment per unit of depth than a vertical one. The surface enters through the boundary conditions. At the top, the light going down in direction μ is the light that came in from outside plus the fraction $R_F(\mu)$ of the light coming up at the mirrored angle, where R_F is the boundary reflectance seen from inside. For a binder of index n , every direction with μ below $\mu_c = \sqrt{1 - 1/n^2}$ lies beyond the critical angle and has $R_F = 1$; for $n = 1.5$, $\mu_c = 0.745$, and only light within 42° of the vertical can leave. At the bottom, the ground reflects whatever reaches it.

The two-flux model comes out of equation (10) by adding up the light over each half of the directions, and the quantity to add up is the flux, the power crossing a horizontal plane per unit of its area. A ray at angle θ meets a patch dA of the plane obliquely, and the patch presents to it only the area $dA \cos \theta$, so light of intensity I arriving within a small solid angle $d\Omega$ carries the power $I \cos \theta d\Omega dA$ across the patch. A small solid angle is $d\Omega = \sin \theta d\theta d\phi$, with ϕ the bearing, the horizontal direction of travel, and since $d\mu = -\sin \theta d\theta$ it is also $d\mu d\phi$ in size. Adding over every downward direction, with the bearing contributing a factor 2π because I does not depend on it, gives the downward flux, and the same sum over the upward directions gives the upward one:

$$F_+(z) = 2\pi \int_0^1 I(z, \mu) \mu d\mu, \quad F_-(z) = 2\pi \int_0^1 I(z, -\mu) \mu d\mu. \quad (11)$$

Multiply equation (10) by 2π and integrate it over the downward directions, μ from 0 to 1. The left side becomes dF_+/dz , because the μ the slant put into equation (10) is the same cosine that turns intensity into flux. The first term on the right becomes $-(\sigma_a + \sigma_s)E_+$, with $E_+ = 2\pi \int_0^1 I d\mu$. This has no factor μ and is not the flux. It counts each ray by the light it carries whatever its slant, which is the right count for absorption: a ray crossing the slice dz at a slant is absorbed along the path dz/μ , and its flux $I\mu d\Omega$ times $\sigma_a dz/\mu$ is $\sigma_a I d\Omega dz$, with the μ gone. Write $E_+ = u_+ F_+$, where

$$u_+ = \frac{\int_0^1 I d\mu}{\int_0^1 I \mu d\mu} \quad (12)$$

is the average of $1/\mu$ over the downward light, each direction weighted by the flux it carries: the length of path the downward light travels, on average, per unit of depth. In the last term of equation (10), change the order of the two integrals. For light arriving from a direction μ' , $\frac{1}{2} \int_0^1 p(\mu, \mu') d\mu$ is the share of what the particles scatter out of it that goes into the downward half. Call $\beta(\mu')$ the share that goes into the half the light did not come from, so that downward light keeps $1 - \beta$ of its scattered light going down and upward light sends β of its scattered light down. Averaging β over each half, weighted by intensity, gives a back-scattered share b_+ for the downward light and b_- for the upward, and the integrated equation is

$$\frac{dF_+}{dz} = -(\sigma_a + \sigma_s) E_+ + \sigma_s(1 - b_+) E_+ + \sigma_s b_- E_- = -\sigma_a E_+ - \sigma_s b_+ E_+ + \sigma_s b_- E_-. \quad (13)$$

The downward flux loses what is absorbed and what is scattered back up. Light a particle scatters forward leaves one downward direction for another and is still in the downward flux, so it cancels out. The downward flux gains what the upward light scatters back down. With $E = uF$, and the same steps over the upward half, where the left side comes out as $-dF_-/dz$

because the upward flux grows toward the top,

$$\begin{aligned}\frac{dF_+}{dz} &= -u_+(\sigma_a + b_+\sigma_s)F_+ + u_-b_-\sigma_s F_-, \\ -\frac{dF_-}{dz} &= -u_-(\sigma_a + b_-\sigma_s)F_- + u_+b_+\sigma_s F_+.\end{aligned}\tag{14}$$

Nothing has been approximated yet, but the equations are not closed. The path factors $u_{\pm}$ and the back-scattered shares $b_{\pm}$ depend on how the light is spread over its directions, which is what equation (10) was needed to find, and they change with depth.

Kubelka and Munk closed the equations by assuming that the light is perfectly diffuse, with I the same in every direction of each half. Then equation (12) gives $u_+ = u_- = 1/\frac{1}{2} = 2$, and b_+ and b_- become one number b , the back-scattered share for diffuse light, which belongs to the particles alone. Equations (14) become

$$\begin{aligned}\frac{dF_+}{dz} &= -(K + S)F_+ + SF_-, \\ -\frac{dF_-}{dz} &= -(K + S)F_- + SF_+, \\ K &= 2\sigma_a, \quad S = 2b\sigma_s,\end{aligned}\tag{15}$$

which are the Kubelka–Munk equations, with F_+ and F_- in place of the I and J used above. A particle that scatters equally in every direction sends half of what it scatters into the other half, $b = \frac{1}{2}$, and $S = \sigma_s$; a particle that scatters mostly forward has a smaller b . The 2 in K is the path factor of diffuse light: it crosses a slice along a path twice the slice’s thickness, on average, and so it is absorbed twice as fast per unit of depth as a vertical beam. Where the light is not diffuse, the true u and b differ from these values. Near the top, under the instrument’s nearly vertical beam, u is close to 1; in a glaze that does not scatter, the upward light loses its slanted rays as it rises and its u falls below 2. Other assumptions about the spread of directions give other factors, and Mudgett and Richards, solving equation (10) accurately for pigmented layers, derived empirical relations for K and S that make the two-flux model agree with the accurate solution as nearly as it can [52].

Saunderson’s internal coefficient is the same assumption applied at the surface. Perfectly diffuse light meets the surface from below with the share $2\mu d\mu$ in the directions between μ and $\mu + d\mu$, and the share the surface reflects is

$$k_2 = \int_0^1 R_F(\mu) 2\mu d\mu,\tag{16}$$

which for $n = 1.5$ is 0.596. Of that, $1 - 1/n^2 = 5/9$ comes from the directions beyond the critical angle, all of which are reflected, and the remaining 0.04 from partial reflection of the rest. This is the 0.60 of Section 2.2. The external coefficient k_1 is the boundary reflectance for the instrument’s beam, about 0.04 near normal incidence. Klein’s objection to the formula is that its two coefficients rest on two different assumptions, one directional and one diffuse, and that neither holds exactly for light that is partly both [39].

Equation (10) can be solved as accurately as one likes by replacing the integral over directions with a sum over a chosen set of directions, usually the points of a Gauss quadrature. It becomes a set of linear differential equations in the intensities along those directions, whose solution in a uniform layer is a sum of exponentials in depth, and the boundary reflectance is applied

direction by direction at each boundary. This is the method of discrete ordinates set out by Chandrasekhar [9]; in the literature on paint and paper it is called the many-flux method. Mudgett and Richards applied it to pigmented layers and compared it with the two-flux model and with a four-flux model, which adds a collimated beam going down and one coming back to the two diffuse fluxes [52]. The two-flux model gave excellent results when the absorption was small compared with the scattering and the layer's optical thickness was more than 5. The four-flux model did well at any thickness under collimated light, even with strong absorption. Vargas and Niklasson showed formally that the Kubelka–Munk model is a good approximation for optically thick films of particles that absorb weakly or not at all [74]. Klein's preference for three or more fluxes in translucent layers [39] agrees with both.

The tints in this paper lie mostly where the two-flux model is good. A tint is a thick layer whose scattering comes mainly from titanium white, which at a normal loading scatters several hundred times per millimeter (Section 2.4); the instrument's beam loses its direction within the first few scattering lengths, and below that the light is close to diffuse. In the bands a pigment passes, the absorption is small compared with the scattering, the case Mudgett and Richards found the two-flux model handles well. In the bands it absorbs strongly the ratio is not small, and that is where the model is least exact; the calibration, done on the same kind of layer, takes up part of the error there. The direct test is measurement. The modeled tints come within $0.85 \Delta E_{00}$ on average of the 26 ladders Okumura measured (Section 2.6), and whatever the two-flux approximation costs in a tint is inside that figure.

The glaze is the opposite case. A film of transparent pigment over white scatters almost nothing, so the light in it is never made diffuse by scattering. Light from the ground does start out diffuse, since the white scatters it in every direction, but it does not stay so. On the way up, a ray at angle θ crosses a film of thickness d along a path d/μ , so the slanted rays are absorbed more than the steep ones, and only the steep ones, those within 42° of the vertical, can leave. The rest are turned back by total internal reflection and cross the film again at the same slant. The light that leaves on its first try has crossed the film along a path 1.14 times its thickness on average, against 2 for diffuse light; the light turned back crosses it at least twice more, each time at a slant. A film that does not scatter is simple enough to work out direction by direction. Let the film's absorption coefficient along a ray be α , so that its optical depth is $\tau = \alpha d$; let the ground be the model's white, a diffuse reflector of reflectance R_g seen from inside the binder; and let the instrument's beam come in at 8° , which bends to $\mu_0 = 0.996$ inside. A sphere instrument lights the sample diffusely and reads it at 8° , and by reciprocity that gives the same reflectance as lighting it at 8° and collecting every direction. The beam reaches the ground with the fraction $(1 - k_1) e^{-\tau/\mu_0}$ of its light. Of the diffuse light the ground sends up, the fraction that leaves through the top on its first try, and the fraction that is reflected at the top and gets back down to the ground, are

$$U(\tau) = \int_0^1 (1 - R_F(\mu)) e^{-\tau/\mu} 2\mu d\mu, \quad D(\tau) = \int_0^1 R_F(\mu) e^{-2\tau/\mu} 2\mu d\mu, \quad (17)$$

and adding up the light over its round trips between the ground and the surface gives

$$R = k_1 + \frac{(1 - k_1) e^{-\tau/\mu_0} R_g U(\tau)}{1 - R_g D(\tau)}. \quad (18)$$

For a film of no thickness, $U = 1 - k_2$ and $D = k_2$ by equation (16), and equation (18) is Saunderson's formula over the bare ground. The two-flux glaze of Section 3.6 replaces every

crossing of the film by the same exponential, e^{-uK} each way with K the coefficient for diffuse light; equation (18) keeps the spread of paths.

The spread is what changes the color. A change in the mean path alone would only change how thick a film is needed for a given lightness, and a glaze is compared with a tint at equal lightness. A spread of paths makes the reflectance an average of exponentials, $\langle e^{-\alpha L} \rangle$ over the paths L , and in a band the pigment absorbs strongly that average is ruled by the shortest paths, which let through far more light than a single path of the mean length would. At equal lightness the glaze worked out direction by direction reflects more in its absorbed band and is less pure. Table 2 gives the numbers for the four paints of Figure 18, computed both ways from the same absorption spectra, with the thickness set to reach each lightness and the same surface reflection at the top, $k_1 = 0.035$, so that only the treatment of the light inside the film differs.

Table 2: Glazes over white at $L^* = 50$ and 65 computed two ways, by the two-flux model of Section 3.6 and direction by direction with equation (18). The tint is the same paint mixed with white to the same lightness. The last column is the share of the glaze’s lead over the tint that the direction-by-direction calculation removes.

paint	L^*	tint C_{ab}^*	glaze C_{ab}^*		lead removed
			two-flux	by direction	
Quinacridone magenta	50	55.2	86.7	81.3	17%
	65	46.3	67.4	62.4	24%
Phthalo green	50	45.8	76.0	72.0	13%
	65	46.8	82.1	75.5	19%
Dioxazine purple	50	44.4	71.8	65.6	23%
	65	34.6	49.7	46.4	22%
Burnt sienna	50	24.9	49.5	43.3	25%
	65	21.6	41.8	35.4	32%

The glaze loses 3 to 7 units of chroma, and its lead over the tint shrinks by 13 to 32 percent, about a fifth on average. At a lightness of 50 the quinacridone magenta glaze has a chroma of 81 against the tint’s 55, where the two-flux model gave 87; phthalo green has 72 against 46, where it gave 76. The lead is 12 to 29 units direction by direction, against 15 to 35 by the two-flux model. The two-flux glaze moves by about as much with the surface coefficient alone: with k_2 moved from 0.4 to 0.7, the magenta glaze at $L^* = 50$ goes from 91 to 84 and the phthalo green from 79 to 74. Both calculations leave out the little scattering a real glaze does, at its particles and where it meets the ground, which would take a little more from the glaze, and neither has been checked against a measured glaze.

The rest of the paper keeps the two-flux model with Saunderson’s correction for every layer, glazes included. It needs two numbers per wavelength for each paint and mixes paints by adding them, and it is the model the coefficients were extracted with, so that the extraction and the prediction share their errors. A many-flux model would need the phase function of each pigment, which reflectance measurements do not give, and a calibration of its own. For the tints and the mixtures with white, which make up most of Parts 3 and 4, the error this brings in lies inside the model’s measured accuracy of about one unit of color difference. For the glazes it is a few units of chroma, about a fifth of the gap between glaze and tint, and always in the same direction,

so the glaze numbers of Section 3.6 are best read as upper bounds; the glaze stays far purer than the tint at both lightnesses compared. The masstones of the most transparent paints are a separate matter. Their trouble is a film that does not hide its card (Section 2.6), and no model of the light inside the film fixes that without a measurement of the same film over black.

Scattering and hiding (Section 2.4). Light travels a distance of the order of $1/S$ in a paint before it is turned around, and a layer hides its ground once its thickness is several times that distance, so that light reaching the ground and returning is a small fraction of the whole. For titanium white at a normal pigment loading S is several hundred per millimeter, and for a phthalocyanine it is a few per millimeter [43]. *Hiding power* in the trade is the area a unit quantity of paint will cover to a stated contrast ratio over black and white; it rises with S and also with K . The scattering strengths of Figure 10(a) are per gram of paint and relative to the white's. Titan buff scatters about as much as the white; carbon black, diarylide yellow, naphthol red and chromium oxide a quarter to a third as much; yellow ochre and red oxide a sixth; the siennas and umbers a twentieth to a tenth; ultramarine and cobalt blue a fiftieth to a twentieth; the phthalocyanines and anthraquinone blue a hundredth or less. In panel (b), pyrrole red starts at a lightness of 43 and a chroma of 69 and loses chroma with every addition of white, while quinacridone magenta starts at 32 and 30 and rises to a chroma of 55 near one part white to two of paint. In panel (c), pyrrole red reflects 76 to 88 percent of the light above 640 nm, and quinacridone magenta reflects no more than 61 percent at the far red end. Scattering varies across the spectrum because the real part of a material's refractive index changes fastest where it absorbs. The Lawrence Berkeley measurements of phthalocyanine blue show its scattering coefficient peaking near 720 nm, just past the red edge of its absorption band, and Klein notes that for colored pigments the scattering coefficient tends to follow the reflectance curve [43, 39]. Okumura found the same kind of spectral change in scattering in his tint ladders of the Golden paints, most clearly for phthalo green, where the shape of the K/S curve changes with the concentration of paint [59].

Where pigment colors come from (Section 2.5). A semiconductor absorbs every photon with more energy than its band gap and none with less. Cadmium sulfide has a gap of 2.4 electron volts, the energy of light at about 515 nm, and the sulfoselenides have smaller gaps [57]. In Figure 11, cadmium yellow light rises from 5 to 90 percent between 480 and 540 nm and cadmium red light between 560 and 620 nm. The iron oxides are colored by the Fe^{3+} ion: transitions within its d electrons, which are weak, and a charge-transfer absorption in the ultraviolet and blue, which is strong [68]. Goethite is the hydrated oxide and hematite the anhydrous one, and calcining converts the first to the second. Yellow oxide and raw sienna peak around 600 nm and fall off a little in the red, red oxide and burnt sienna climb through the red, and the umbers stay below 10 percent everywhere. Cobalt blue is cobalt aluminate, with Co^{2+} in a tetrahedral site whose d electrons absorb the orange and red; cerulean and cobalt teal are cobalt in chromium and titanium oxides; chromium oxide is colored by Cr^{3+} [57]. Cobalt blue reflects a band around 460 nm and rises again above 650 nm; cobalt teal reflects a broad band from 450 to 550 nm; chromium oxide reflects a modest band at 540 nm and more in the far red. Ultramarine's color is the S_3^- radical ion, which absorbs a broad band centered near 600 nm; it reflects a narrow band at 450 nm, and its refractive index is about 1.5 [8]. In the organic pigments the color comes from a conjugated system of double bonds. Copper phthalocyanine absorbs strongly from 550 to 750 nm and weakly below 500, and the phthalocyanine curves have their small bump at 450 or 500 nm.

The quinacridones absorb from 400 to about 600 nm with the edge placed by the substituents; the azo and arylide yellows have their edges at 490 to 520 nm; pyrrole red, diketopyrrolopyrrole, has its edge at 600 nm [57, 25]. These pigments have particles of about $0.1\ \mu\text{m}$ [31], and their refractive indices, 1.6 to 2, are not especially close to the binder's: Okumura gives 1.66 for an arylide yellow against 1.48 for the acrylic binder [59]. Titanium dioxide's ultraviolet absorption has a tail that begins at about 410 nm [8].

The model and its fit (Section 2.6). Golden measured 78 of its Heavy Body acrylics as 10 mil wet drawdowns over a white card, dried to about 6 mil, with an integrating sphere that includes the specular reflection, under D65 for the 10° observer, from 400 to 700 nm at 10 nm intervals [24]. Golden's pigment chart gives the pigment and opacity rating of each paint and, for its titanium white, a lightness of 98.3 [25]. The white's spectrum was measured at RIT for the Art-SI library, on nine samples of Golden titanium white on gessoed canvas and board, at 45° from the mirror direction [71]; it is the rutile curve of Figure 19, flat across the visible with a steep absorption edge below 420 nm. Okumura painted his ladders of 26 Golden Matte Fluid acrylics with Golden titanium white, at 10 to 100 percent paint by weight, and published the lightness, chroma and hue of every step [59]. The Matte Fluid and Heavy Body masstones agree in lightness within about two units, with the one exception of hansa yellow medium, whose ladder is Okumura's Hansa Yellow Opaque.

From each measured masstone the surface is removed with equation (9), with $k_1 = 0.035$ and $k_2 = 0.60$, and the internal reflectance is converted to the masstone ratio $m(\lambda) = K/S$ by equation (8). Paint i is assigned a scattering coefficient relative to the white's, $S_i(\lambda) = s_i \exp(\beta_i x + \gamma_i x^2)$ with $x = (\lambda - 550)/150$, so that s_i is its scattering strength per gram at 550 nm and β_i, γ_i let the scattering tilt and curve across the spectrum, and an absorption coefficient $K_i = S_i m_i$. Where the masstone lies on the surface floor, with an internal reflectance below about one percent, the measured ratio is unreliable and is multiplied by $\exp(a_i + b_i x)$. The white has $S = 1$ and an absorption K_w from its own measured reflectance. A mixture of amounts c_i by weight has

$$\frac{K}{S} = \frac{\sum_i c_i S_i m_i + c_w K_w}{\sum_i c_i S_i + c_w}, \quad (19)$$

which is Duncan's two-constant form of the law [22]; in the single-constant form only the white scatters, and each colorant brings only its absorption. The mixture's reflectance follows from equation (8) and the surface is put back with equation (9), so that the result is what Golden's instrument would read. Colors are then computed for D65 and the 2° observer. The five numbers $s_i, \beta_i, \gamma_i, a_i, b_i$ were fitted by least squares to the measured CIELAB coordinates of each step of Okumura's ladder, for the 26 paints that have one. They are in the file `pigment.params.csv` that comes with the paper, one line per paint, left empty for the paints that have no ladder.

Over the 26 ladders the mean error is $0.85\ \Delta E_{00}$; the median paint is fitted to 0.64 and the worst, hansa yellow medium, to 2.4. Okumura's own test of his model on 27 two-paint mixtures found a mean error of 2.2 and a worst of 8, for mixtures of a translucent yellow with ultramarine [59]. Quinacridone magenta's chroma rises from 30 to 55 and falls back to 20 along the ladder, and phthalo blue's from 24 to 44 and back, and the model reproduces both the position and the height of each peak. Mohammadi and Berns, in a separate study of artists' acrylics, found that the two-constant law reproduced a ladder of cobalt blue to within 0.6 percent in reflectance from the masstone and a single tint [51], and Okumura found the same law fitted all his ladders

to a mean of $0.3 \Delta E_{00}$ when the coefficients were free at every wavelength [59]. This paper’s model is more constrained, since it takes the shape of the absorption from the masstone, and it is correspondingly a little less exact. The fitted β_i and γ_i are poorly constrained in the bands a paint absorbs, several of them sit at the bounds allowed in the fit, and for the phthalos and pyrrole red they make the scattering in the red many times the white’s, while at 550 nm the phthalos scatter about a hundredth as much as the white. The fitted shapes move the model’s masstones away from the measured ones by less than $1 \Delta E_{00}$ for most paints and by about 5 for ultramarine.

3 How paints mix

Part 2 ended with a model that predicts the color of any mixture of the 26 calibrated Golden paints, the ones whose tints with white Okumura measured, together with titanium white. This part puts the model to work on the questions a painter meets at the palette. Most of the figures here are computed with it. Wherever Okumura measured the same mixture, his measurement is drawn beside the prediction, and Figure 19(a) shows his measurements alone. The masstone colors quoted in this part are the model’s, which can sit a little away from the measured ones (Section 2.6).

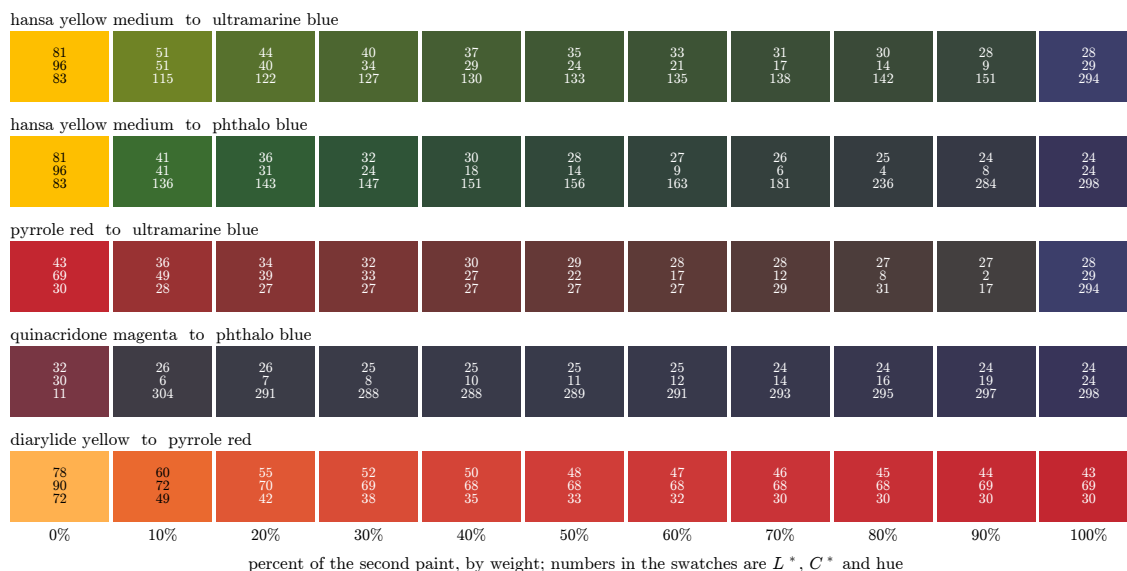
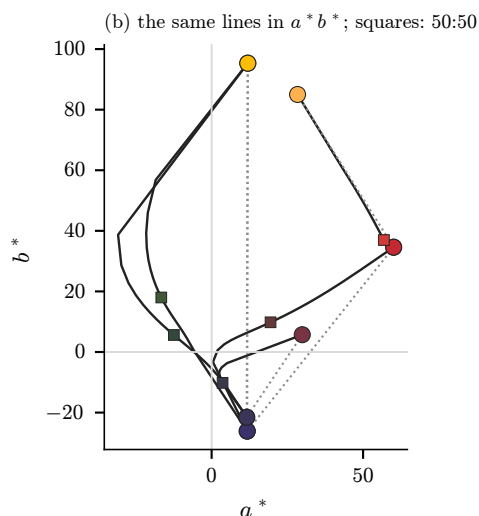
We start with what happens along the way from one paint to another, and why transparent and opaque paints mix so differently. Then come the effects of white: why reds turn pink, why a dark transparent paint comes alive in a tint, when a mixture can be more vivid than both of its paints, why a glaze is not a tint, and what the white itself adds. The later subsections test the six-paint split-primary palette, mix every pair from a set of paints around the hue circle, ask whether black deadens a color, and end with how the paint industry matches colors.

3.1. Mixing lines. Mix two paints in equal steps by weight and the colors do not come out in equal steps. A tenth of phthalo blue stirred into hansa yellow medium takes the yellow from a lightness of 81 down to 41, and the other nine tenths of blue take it only to 24. The path from one paint to the other is not straight either. It bends toward gray, so the half-and-half mixture of two vivid paints can be dull, and a red and a blue can pass through a color with no hue at all on their way to each other. We call the series of colors between two paints their mixing line, and this subsection explains its shape.

Figure 13(a) mixes five pairs in steps of ten percent. With hansa yellow medium and ultramarine, the first tenth of blue makes more of the change than the next eight tenths together, and the greens after it grow darker and grayer as the blue goes in. Pyrrole red and ultramarine never pass through a violet. The red only darkens and dulls until, at nine parts blue to one of red, it is a dark gray, and the blue shows itself only at the last step. Quinacridone magenta and phthalo blue are dark the whole way, since both are dark in the tube. The one line that stays vivid in the middle runs from diarylide yellow to pyrrole red, two semi-opaque paints of neighboring hue. Both reflect the same long wavelengths, and they differ only in where their reflectance climbs from dark to bright.

Panel (b) draws the same lines on the color map of Section 1.7, where the center is gray and the distance from the center is chroma, each with a dotted straight line joining its two ends for comparison. None of the mixing lines follows its straight line. The two lines from yellow to blue bow outward through the greens compared with their straight lines, and that bow is what

(a) five mixing lines, in steps of 10 percent by weight



(c) black into white

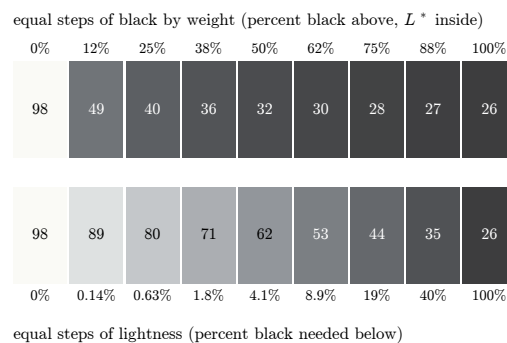


Figure 13: Mixing lines. (a) Five pairs of Golden paints mixed in steps of ten percent by weight, with the lightness, chroma and hue angle of each step. (b) The same five lines on the color map of Section 1.7; the dotted lines join each pair directly, and the squares mark the half-and-half mixtures. (c) Carbon black stirred into titanium white, in equal steps of weight and in steps that look equal in lightness, with the amount of black each of those steps needs.

makes a green from a yellow and a blue possible at all. Every green on them is much duller than the yellow, and past the first few steps it is duller than the blue as well. The lines from red to blue and from magenta to blue cut straight through the gray center. The squares mark the half-and-half mixtures, and they sit far from the middle of their lines. Half hansa yellow medium and half phthalo blue lands two thirds of the way along, as a dark, grayish green.

Black stirred into white, in panel (c), is the plainest case. To make steps that look equal in lightness, each step needs about twice as much black as the one before. That comes mainly from the paint: near white, the first trace of anything that absorbs takes away far more light than any later addition does (Section 2.1), and the eye's scale of lightness adds a little to it. The same steep start is why the first tenth of a dark paint counts for so much in the lines of panel (a).

To see where the rest comes from, recall what decides the color of a thick layer of paint. For each color of light, it is how strongly the paint absorbs that color compared with how strongly it scatters it back out. Color scientists write this ratio K/S , K for absorption and S for scattering, and a masstone shows a paint's own K/S at every wavelength. When paints are stirred together, their absorptions simply add up, and so do their scatterings [22]. The mixture's ratio is its total absorption over its total scattering, and that always lands somewhere between the paints' own ratios. It is a kind of average, though not an average by weight. Each paint's say in it is its share of the mixture's scattering. A paint that scatters a lot gets a large say, and a transparent paint, which scatters little, gets a small one.

Principle 3.1. *Paints mix as an average of their K/S , each paint counted by its share of the mixture's scattering. They do not mix as an average of their reflectances or of their colors.*

That small say does not make a transparent paint weak. In the colors it absorbs, its masstone is nearly black, so its own K/S there is enormous, and a small share of something enormous is still large. It comes down to how strongly the paint absorbs per gram, set against all the scattering in the mixture, and that is its tinting strength. Phthalo blue absorbs red light very strongly per gram and, in the middle of the spectrum, scatters about a hundredth as much as the white, so a tenth of it takes hansa yellow medium to a lightness of 41. Ultramarine absorbs less per gram and scatters more, and a tenth of it takes the same yellow only to 51.

Mixing lines bend toward gray for a related reason. In the colors that one paint absorbs and the other reflects, the mixture takes on some of the absorption. Each paint's bright colors are dimmed by its partner, so the mixture is duller than a color halfway between the two. The less the two paints reflect in common, the deeper the sag. A red and a blue from opposite sides of the hue circle share almost nothing, and their line runs right through gray, as pyrrole red and ultramarine did above. Why no choice of color coordinates can straighten these lines is taken up in [49].

Because the mixture's K/S is an average, it never goes outside the range of the paints' own. Part 4 relies on this, and a second consequence, about scattering, goes with it.

Fact 3.2. *In the mixing law used here, at every wavelength a mixture's K/S lies between the K/S values of the paints in it. Two paints with the same masstone whose scattering differs only in strength, one a fixed multiple of the other at every wavelength, make the same colors with any partner; the weaker one just takes more paint to reach each color.*

The reason for the second half is simple. If the two paints have the same masstone, the one that scatters more also absorbs more per gram, in the same proportion, so a gram of it carries the

absorption and the scattering of several grams of the weaker one. Any mixture made with the strong paint can be made with the weak one by using more of it. Paints whose scattering is spread differently across the spectrum are another case, and their mixtures can differ in color. Section 3.12 writes the mixing law in symbols and does the algebra behind the fact.

3.2. Subtractive and additive. There are two simple ways to combine colors. Lights add: shine two lights on one spot and you get the sum of the two. Filters subtract: light passing through two filters in a row keeps only what both let through. Paint mixtures sit somewhere between. Light that enters a mixture bounces from particle to particle, and on the way both pigments absorb some of it, which is the subtracting part. A particle that scatters strongly, though, turns light around before it has gone far, so some light comes back out having met only one pigment, which is the adding part. The more one paint scatters, the more of the light its partner would have absorbed gets sent back out.

So mixtures of opaque paints come out lighter and grayer, closer to an average of the two paints, and mixtures of transparent paints, which scatter almost nothing, come out dark, because whatever either paint absorbs is lost.

A thought experiment shows the range, one that no real pair of paints allows, since no two pigments absorb exactly alike. In Figure 14(a), hansa yellow medium is mixed half and half with an imaginary blue that absorbs exactly like phthalo blue but whose scattering we set by hand. At first it scatters nothing, which makes it a dye dissolved in the binder. Then it is given a few times the scattering of the real phthalo, and then a little more than opaque chromium oxide has. The dashed curve beside each mixture is the plain average of the two paints' reflectances. That average is what fine dots of the two side by side would give, the fully additive case.

With the dye, the yellow's red light is simply gone: where the yellow alone reflects most of it, the mixture reflects almost none, and the result is a dark green. As the blue is given more scattering, it grows paler on its own, from black to a pale blue, and the mixture climbs toward the average in the band of wavelengths the blue absorbs. Panel (b) follows this up to a blue that scatters as much as the white. In that band the mixture keeps less than a tenth of the average's light at the start and more than half at the end. The green turns gray along the way and ends as a dull violet, because a blue that scatters as much as the white is a weak, pale blue, and the mixture is mostly that pale blue with some of the yellow's red let back in.

Each imaginary blue is really a different paint, since its masstone pales as its scattering grows, so none of this goes against Fact 3.2. A real opaque pigment shows its opacity in its masstone already.

Real pairs behave as the thought experiment predicts. Panel (c) takes four pairs of hues and makes each pair twice, once from transparent paints and once from opaque or semi-opaque ones, half and half by weight. Semi-transparent hansa yellow medium with transparent phthalo blue gives a dark green that keeps only about a tenth of the average's light in the band the phthalo absorbs. Diarylide yellow with cerulean blue, both semi-opaque, keeps nearly half in the band the cerulean absorbs, and makes a lighter green. In all four pairs the opaque version comes several times closer to the average in the band that matters.

How vivid a mixture is, as opposed to how light, depends on what both paints reflect in the colors between them, which Section 3.8 takes up at length. Hansa yellow medium makes a much more vivid orange with semi-opaque pyrrole red than with transparent quinacridone crimson, a



Figure 14: Between subtracting and adding. (a) Hansa yellow medium mixed half and half with an imaginary blue that absorbs like phthalo blue, given three amounts of scattering; the dashed curves are the plain averages of the two paints, the fully additive case. (b) The same at six amounts of scattering: the blue alone, the mixture, the average, and the share of the average's light the mixture keeps where the blue absorbs. (c) Four real pairs of similar hues, each made once from transparent or semi-transparent paints and once from opaque or semi-opaque ones by Golden's ratings, half and half by weight, with the same comparison.

chroma of 64 against 46, because the pyrrole red already reflects the orange the mixture needs. Transparent pigments make dark, rich masstones and glazes, but being transparent does not make them cleaner mixers.

The share of the scattering decides how subtractive a mixture is. Take a band where one paint absorbs strongly and its partner hardly absorbs at all. If the partner supplies none of the mixture's scattering, the band is exactly as dark as in the absorbing paint alone, and the mixing there is fully subtractive. If the partner, or a white in the mix, supplies nearly all of it, the band is nearly as bright as in the partner alone, and the mixing there is additive. In between, the absorbing paint's K/S in that band counts in proportion to the pigment's share of the mixture's scattering: if it supplies a tenth of the scattering, its K/S there is cut to a tenth.

Principle 3.3. *In the band a pigment absorbs, its absorption counts in a mixture in proportion to the pigment's share of the mixture's scattering. Scattering supplied by the other ingredients, white included, returns the light that the pigment would have absorbed. Opaque partners make a mixture additive; transparent partners leave it subtractive.*

The same rule shows why an opaque blue's dark band is easier to lift than a transparent blue's. An opaque pigment's own scattering already returns some light in the band it absorbs, so its masstone is not black there: in the model, cobalt blue still sends back about an eighth of the red light that gets into it. Phthalo blue sends back only a few percent. Suppose a partner supplies nine tenths of the scattering, which cuts each blue's K/S in its dark band to a tenth. Cobalt's band then comes back to a middle tone, nearly half the light, while phthalo's stays dark. A transparent pigment's dark band stays dark in any mixture in which it keeps even a tenth of the scattering.

Painting manuals put this in words. Briggs calls paint mixing a combination of subtractive mixing and additive averaging, with opaque pigments leaning toward the second because much of their light is returned by particles of one pigment alone [5]. Berns gives the two-constant law as the form of this in numbers, with the single-constant law, in which the white does all the scattering, as the fully subtractive limit [3], and the paint industry gives every pigment its own absorption and scattering for this reason [39]. Purely subtractive mixing does exist, in filters or glazes laid one over another with nothing scattering between them. A mixture of pigments in paint is never quite that, since even a dye in a white has the white's scattering to return some of the light.

Optical mixing, dots of two paints too small for the eye to separate, is the fully additive case, and it does not do what the pointillists' textbooks say either. The eye averages the two reflectances, the dashed curves of panel (a), and since the blues and greens on a palette are dark, the lighter paint dominates the average. Dots of hansa yellow medium and phthalo blue average to a dull yellow, where the stirred mixture of the same two paints is a dark green. Dots of pyrrole red and phthalo green average to a red-brown, where the stirred mixture is nearly gray. From these pairs optical mixing makes neither greens nor grays, only a paler, duller version of the lighter paint.

3.3. Why red paints turn pink with white. A red paint lightened with white does not stay a lighter red. It turns pink: its hue slides toward magenta, and the more white, the further it slides. The cause is in the red's own reflectance. A vivid red already reflects nearly all of the light at the long, red end of the spectrum, so white has nothing to add there. White brings back instead the blue and violet light the red had been absorbing, and red light with some blue light in it is what the eye sees as magenta, or, in a pale tint, pink.

Figure 15(a) follows the hue of five reds as titanium white is added. Hue is measured as an angle around the color circle. Zero degrees is a pinkish red, larger angles lean toward orange and then yellow, and angles just below zero, written as the high three hundreds, lean toward magenta. Pyrrole red, an orange-leaning red at 30 degrees in masstone, ends near 4 in a pale tint, which is a rose. Naphthol red and the two quinacridones go past zero into the magentas. Okumura measured real tint ladders of all five, and his measurements agree with the model on the direction of every shift and roughly on its size [59].

Red oxide, an earth red, moves the least, from 36 degrees to 24. Its reflectance does not jump from dark to bright at one wavelength the way pyrrole red's does. It climbs gradually through the yellow and orange, and white opens that gradual slope about as fast as it opens the blue, so the tint gains yellowish light along with the blue and turns much less.

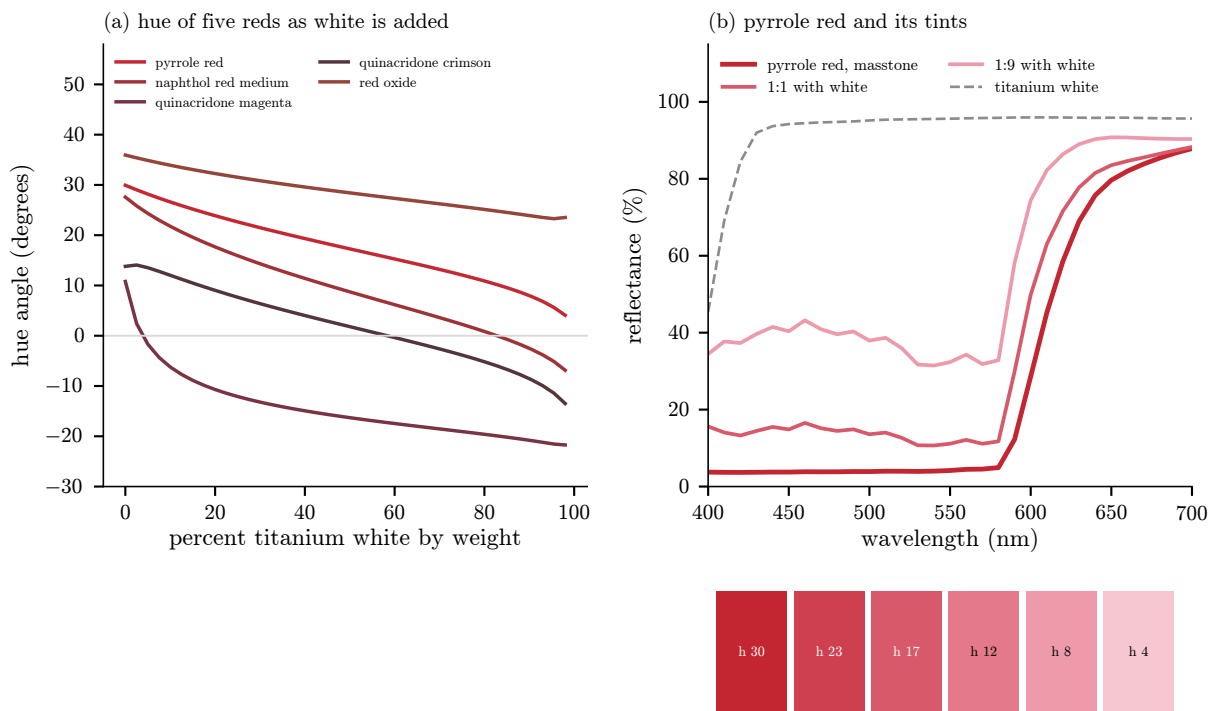


Figure 15: Why reds turn pink. (a) The hue angle of five Golden reds as titanium white is added by weight. (b) The reflectance of pyrrole red in masstone and in two tints, with the white's own; the swatches along the bottom are the tint ladder, with the hue of each step.

Pyrrole red's reflectance, in panel (b), shows where the new light comes from. In masstone the paint reflects most of the red light and almost none of the rest, only the few percent of the surface reflection. Mixed half and half with white, its red barely changes, since it was already close to the white's own level, but its blue and green rise from 4 percent to 13. At one part red to nine of white they reach about a third or more, highest at the blue end. The tint is still a red, since the long wavelengths still dominate, but it is a red with a good deal of blue in it.

On the paint's side, this is the share-of-scattering rule of Section 3.2 with white as the partner. In the blue, pyrrole red absorbs strongly and, in the model, scatters only about a hundredth as much as the white, and in the green not much more; its scattering rises toward the red, where

it reflects. Even at half white nearly all the scattering in the blue comes from the white, and the blue comes back quickly. How little the red scatters in the blue is uncertain (Section 2.6), but scattering that rises toward the red, just past the colors a pigment absorbs, is what colored pigments do (Section 2.4). The white also scatters blue light more strongly than red, which helps.

On the eye's side, the light the white brings back is blue, violet and some green, most of it at the blue end, with a little orange near the edge of the red's band. The blue and violet are what the S cones catch, so they feed the blue side of the yellow-blue channel of Section 1.3 and pull the color away from yellow. The green pulls the red-green channel toward green, but the violet and orange light pull it back toward red, so the tint loses its yellowish lean much faster than its redness. A red that leans toward blue is a magenta, or, pale, a pink.

3.4. Why transparent pigments gain chroma with white. Squeeze out quinacridone magenta, phthalo green or dioxazine purple and the paint looks almost black. Mix in some white and the color appears: quinacridone magenta, a dull dark red in the tube, turns into a vivid pink-red with nearly twice the chroma of the masstone. Keep adding white and the tint gets lighter but weaker, until it is a pastel. The color of these paints first rises and then falls as white is added. Opaque and light paints behave differently. Pyrrole red and hansa yellow medium are at their most vivid straight from the tube, and every addition of white makes them paler and duller.

The trouble with a dark transparent paint is that it absorbs too well. Quinacridone magenta absorbs green light strongly and red light only weakly, and that difference is what makes it a red. In a thick layer, though, even the weak absorption adds up. A particle of this pigment barely scatters, so the red light travels a long way into the paint before anything turns it around, and on that long trip a good part of it is absorbed as well. The masstone is very dark in the green and only part of the way up in the red, and with so little contrast between the two its color is muted.

White gives the light a short way back out. Its particles scatter strongly, so in a tint the light is turned around soon after it enters. The red light, which the magenta absorbs only a little, now comes back nearly whole. The green light is still mostly lost, because the magenta absorbs it so strongly that even a short trip is enough to remove it. Red comes back bright while green stays dark, and the eye reads that contrast as a vivid color.

Adding more white changes the balance. Once nearly all of the red is getting back out, more white cannot make the red any brighter; it can only let more of the green escape. As the green catches up, the contrast shrinks and the tint fades toward white. The color is most vivid in between, where the red has nearly reached its brightest and the green has barely begun to rise. For quinacridone magenta that happens at about one part white to two of paint.

Principle 3.4. *A dark transparent paint is most vivid in a tint. White lets the light the paint passes escape before the light it absorbs, so the color grows more vivid until the passed light is close to its brightest, and fades after that.*

On the curve from Section 2.1, which turns a paint's absorption and scattering into the share of light it reflects, white moves both of quinacridone magenta's colors down by the same factor, as Figure 16(a) shows. The red reaches the steep part first and rises quickly while the green is still on the flat tail; later the red has nowhere left to climb and the green starts to rise. Of the twelve paints in panels (b) and (c), nine rise and fall this way; pyrrole red, red oxide and hansa yellow medium are most vivid straight from the tube. It is not only a prediction of the model: Okumura found it in real paint for every transparent pigment he measured, with phthalo

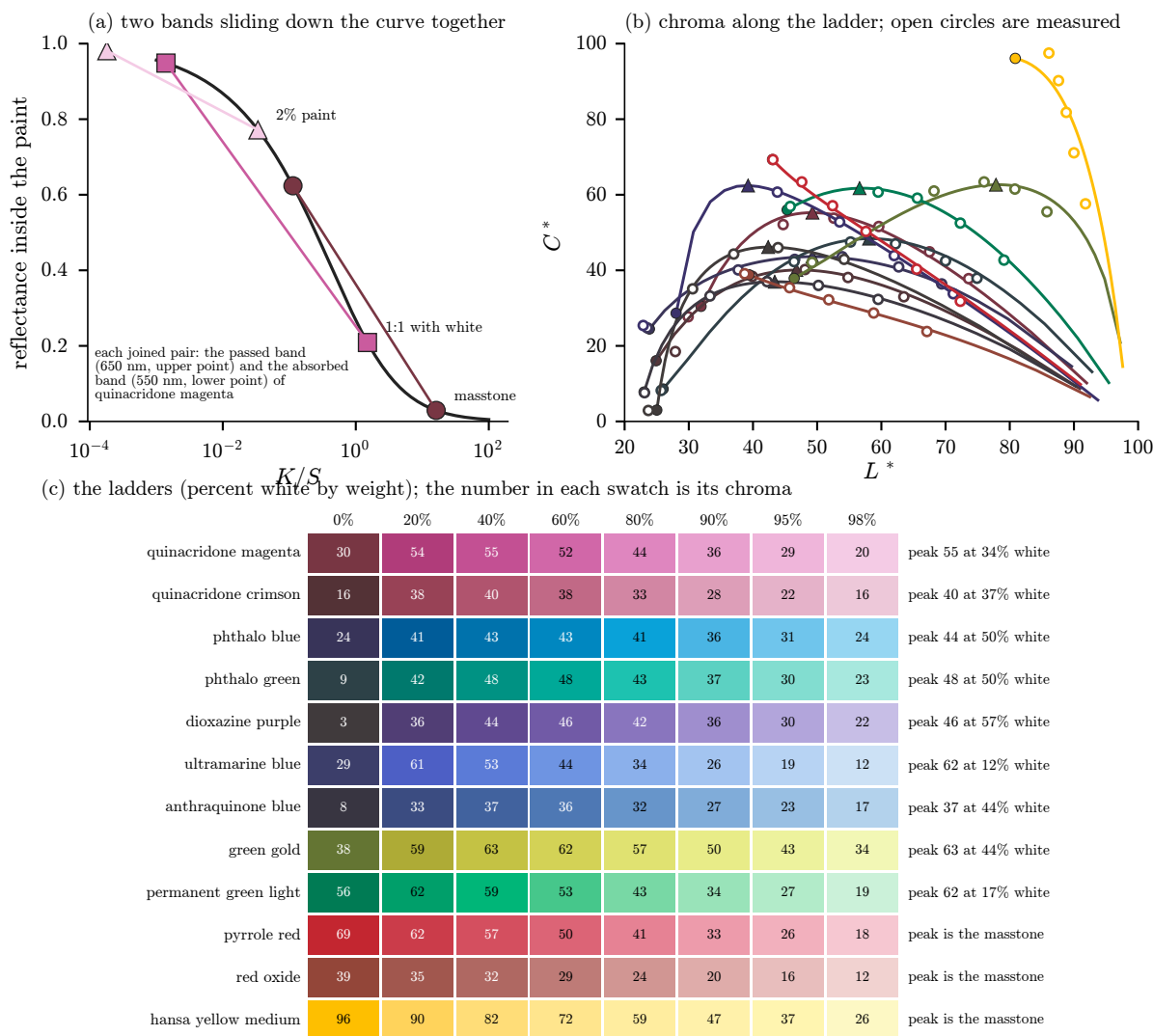


Figure 16: Why transparent paints are most vivid in a tint. (a) Two colors of quinacridone magenta on the curve of Figure 8(c): the red it passes (650 nm) and the green it absorbs (550 nm), in masstone, at equal parts with white, and at two percent paint. White moves both down the curve together, and the red reaches the steep part first. The horizontal scale is logarithmic: each labeled mark is ten times the one before. (b) Chroma against lightness as white is added to twelve paints; the open circles are Okumura's measurements of real paint [59] and the triangles mark the most vivid tint. (c) The same tints as swatches, with the chroma of each.

green, for instance, going from a chroma of 8 in masstone to 48 in its best tint [59]; Golden's own drawdowns show the same thing, with its transparent paints showing their color in tints rather than in masstone [63].

How much white a paint needs before it peaks depends on how dark its masstone is, and Section 3.12 works out where the peak falls. Ultramarine, whose masstone still reflects some blue, peaks with only a little white, while the phthalos need about as much white as paint. A paint that already reflects nearly all of its passed light in masstone has no peak, or only a small one, because white can only raise the light it absorbs. That describes the light paints and most opaque ones: hansa yellow medium, which reflects most of the yellow and red light straight from the tube, fades from the very first addition of white.

A glaze behaves the same way. A thin layer of phthalo green over white is a vivid green and a thick one is nearly black, and the most vivid color is at some thickness in between, because thinning a layer, like adding white, weakens the absorption at every wavelength by the same factor. This is why the transparent paints that look black in the tube are the painter's best glazing colors, and why a color chart of transparent paints has to show a tint or a glaze to show their color at all.

3.5. Mixtures more chromatic than both parents. The painting literature states a firm rule: "the mixture of two paints will always be duller than the more saturated paint" [48]. For a colored paint and white the rule is wrong, and measurements show it. The tint peak of Section 3.4 is a mixture more vivid than both of its parents: in Okumura's ladders dioxazine goes from a chroma of 3 in masstone to 46 with white, while the white itself has a chroma of about 1 [59]. A pale paint that behaves like a white, such as titan buff, does the same in the model, as the third pair in Figure 17 shows. Between two colored paints no exception has been measured, and the model finds only small ones.

The averaging of K/S leaves two ways for a mixture to come out more vivid than either paint, and the appendix follows both in symbols. The first is to clean up stray light. A paint is dulled when it reflects some light outside its main band, the stretch of the spectrum it is meant to reflect. Chromium oxide green is an example: it reflects its green band at about a fifth of the light, and it also leaks a little violet at one end of the spectrum and a little red at the other, which keeps its color muted. A small amount of a partner that is dark at both ends and passes the green could darken the leaks more than it darkens the band. The second way is to brighten the main band. A partner that reflects the main band better than the first paint does lifts it, while each paint's absorption holds down the colors the other lets through. White is the extreme case of this second way, a partner with almost no absorption, and the only one measured to work.

With two colored paints both ways are narrow. A mixture's K/S at every wavelength lies between the two paints' own, so a partner cannot darken the leaks without darkening the main band too, unless it is nearly black outside the main band and passes the main band almost as well as the first paint does. That describes a dark transparent paint of the same or a neighboring hue. Real pigments absorb across broad stretches of the spectrum, so even the best partner takes some of the main band along with the leaks. Two paints from opposite sides of the hue circle can take neither way, because each absorbs the other's main band.

In the model the first way works, though only a little. Ten percent of phthalo green (blue shade), a paint that is nearly black except for a narrow band of blue-green, cuts the leaks of chromium oxide at both ends to half or less and hardly touches its green band, and the chroma rises from 27

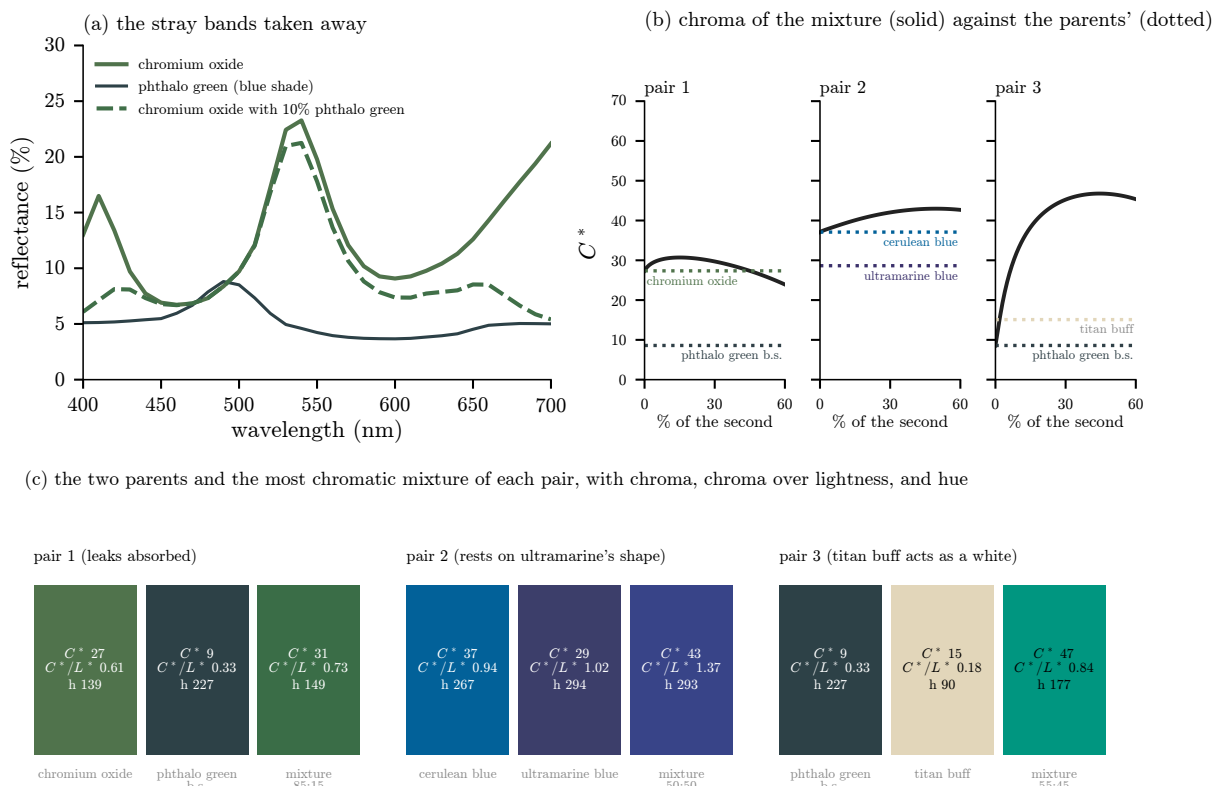


Figure 17: A mixture more vivid than both parents, as the model computes it. (a) The reflectance of chromium oxide, of phthalo green (blue shade), and of chromium oxide with ten percent phthalo green: the leaks at both ends are removed and the green band is kept. (b) Chroma along the mixing line of each pair, one panel per pair, with the two parents' own chroma dotted. (c) The parents and the most vivid mixture of each pair, with their chroma and hue.

to 31 (Figure 17(a)). With more phthalo the chroma falls again, as the phthalo's own blue-green takes over. Across all the pairs of calibrated paints, leaving titan buff aside, only a handful beat both parents by a unit of chroma or more, and none by more than six. The largest, cerulean blue with ultramarine at equal parts, would work the second way, but it rests on how ultramarine's scattering is spread across the spectrum, which its tint ladder does not settle (Section 2.6). Read the ladder another way that fits it about as well, and the gain all but disappears.

Gains this small are within the model's error. When Okumura tested the same kind of model on mixtures of two paints, its predictions were off by about two units of color difference on average and by as much as eight (Section 2.6) [59], as large as the gains themselves, and none of the gains has been measured. With white the exception to the rule is real and large. Between two colored paints, the model allows small exceptions that no one has shown in real paint.

3.6. Glazes against tints. A transparent paint can be made lighter in two ways. You can mix it with white, which makes a tint, or you can thin it and lay it over a white ground, which makes a glaze. At the same lightness they do not give the same color. The glaze is far more

vivid: at a middle lightness quinacridone magenta has a chroma of 55 as a tint and 87 as a glaze, and burnt sienna's chroma doubles.

In a tint, the white's particles turn light back inside the paint layer, including light in the colors the pigment absorbs, and that returned light is exactly what dulls the color (Principle 3.3). In a glaze nothing in the film scatters. Light goes down through the pigment, bounces off the white ground and comes back up through the pigment again. The colors the pigment passes come back nearly whole. The colors it absorbs have to survive two trips through it, and in a thick enough glaze almost none of that light does. A glaze can be made as vivid as the pigment's own absorption allows, at the cost of lightness, and a tint cannot.

Figure 18(a) follows four paints both ways, three transparent ones and burnt sienna, from the masstone up toward white. Along the tint series the chroma rises to the tint peak and then falls. Along the glaze series, from a thick glaze that is nearly the masstone to a thin wash that is nearly the bare ground, it rises to a higher peak and falls more slowly. From the masstone's lightness up to a lightness of about 90 the glaze has the higher chroma, by 20 to 35 units in the middle of the range. Panel (b) sets the two side by side at two lightnesses. The hue differs too: the magenta glaze is slightly more violet than the tint, because the glaze lets through the violet the pigment passes, while in the tint the white dilutes it.

Quinacridone magenta, made both ways to the same middle lightness in panel (c), shows where the difference comes from. In the green, which the pigment absorbs, the tint reflects 10 to 14 percent and the glaze only 5 to 10. In the red, which it passes, the glaze is a little the brighter. The extra green light in the tint is the white's scattering at work, and in the glaze there is nothing to do that work.

The model's glazes are a little too good. A real glaze film scatters slightly at its pigment particles and where it meets the ground, and Section 2.3 found that following the slanting light properly takes a few units of chroma off them. A thick glaze of a strong pigment is also darker than any tint of it. The gap between glaze and tint is several times larger than those corrections. That gap is the physical content of the old distinction between a glaze and a tint, and the reason the transparent pigments are the glazing colors: quinacridone magenta mixed with white gives a pink, while glazed over white it gives a deeper color, more vivid than any of its tints.

3.7. What white does to a hue. Nearly every paint changes hue when white is added, and which way it moves is decided by the pigment. Okumura measured tint ladders, a paint mixed with more and more white, for 26 Golden paints [59]. In them the organic reds swing toward magenta, the blues swing toward cyan, phthalo green turns from a blue masstone into a green tint, and dioxazine goes from a near-black to a violet. The yellows and the earths move the other way round the circle, toward yellow and yellow-green, and by much less.

White brings back the colors a paint absorbs in order of how strongly it absorbs them, the weakest first, and that covers all of these shifts. A pale tint therefore takes on the light that the masstone absorbed least, and its hue moves toward that color. For most pigments that color lies on the blue or green side of the paint's own, and that is where the painter's saying that white cools a color comes from.

The white adds a faint blue cast of its own, far too small to account for these shifts; the end of this subsection measures it.

Figure 19(a) is the measured evidence. For each paint Okumura measured, an arrow runs from

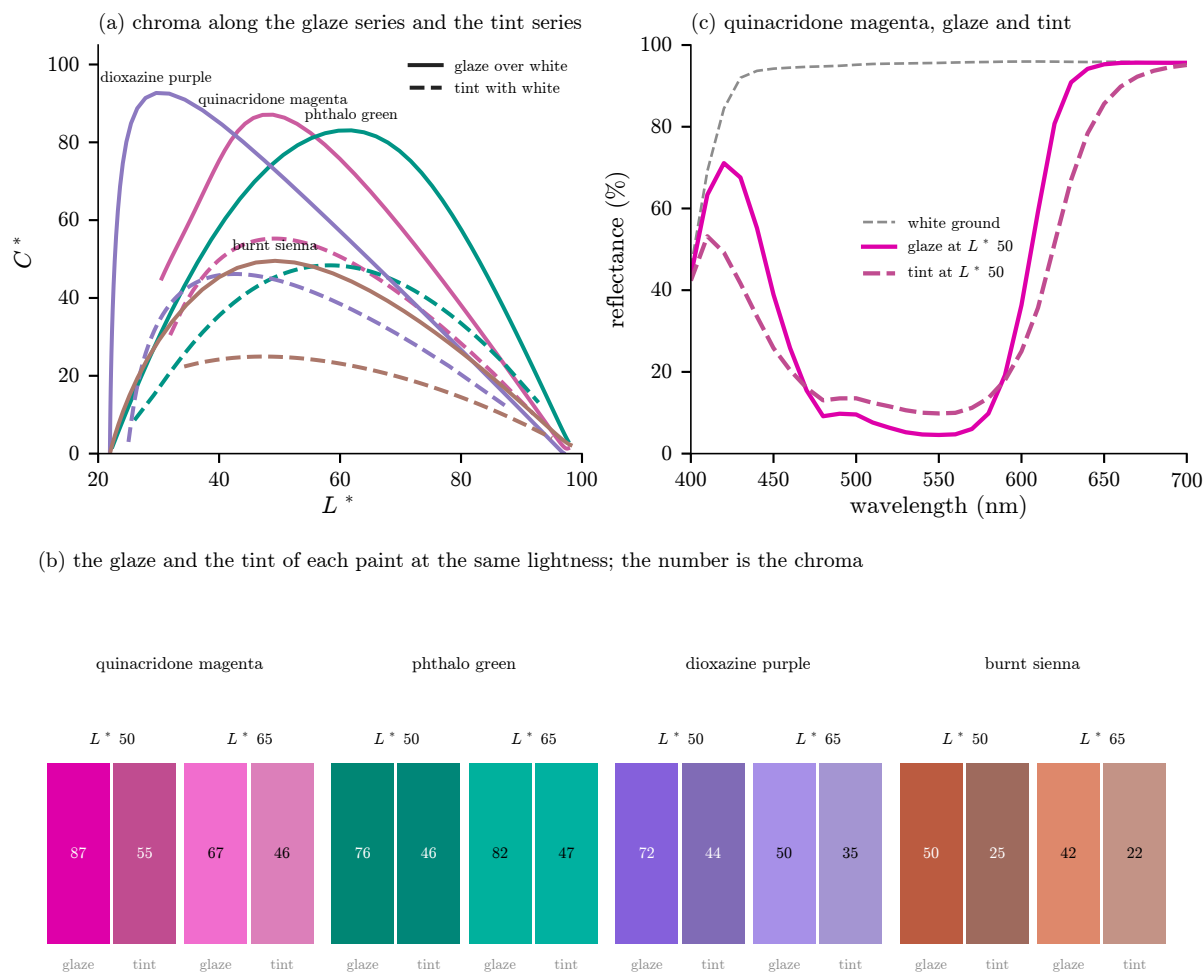


Figure 18: Glazes against tints. (a) Chroma against lightness for three transparent paints and burnt sienna, thinned over a white ground (solid) and mixed with white (dashed), both computed from the same absorption. (b) The glaze and the tint of each paint at lightnesses of 50 and 65, with their chroma. (c) The reflectance of quinacridone magenta as a glaze and as a tint of the same lightness, with the white ground.

the hue of the masstone to the hue of the palest tint. All the reds go toward magenta, the pink shift of the reds. All the blues go toward cyan, and phthalo blue goes furthest, 57 degrees. Its masstone measures as a violet-blue, for all that its name and its tint are greenish, and white turns it into a green-blue. The yellows and the earths go the other way. Red oxide, alone among the earths, turns toward red, and permanent green light does not move at all.

Panel (b) follows three paints that move three different ways. Ultramarine in masstone reflects a narrow band of blue and little else. Just beside that band, in the blue-green, it absorbs only moderately, while across the green, yellow and red it absorbs about five times as strongly. White lifts every color, but the moderately absorbed blue-green comes into view long before the rest, so the tint fills in toward green-blue while the red stays dark, and the hue moves toward cyan.

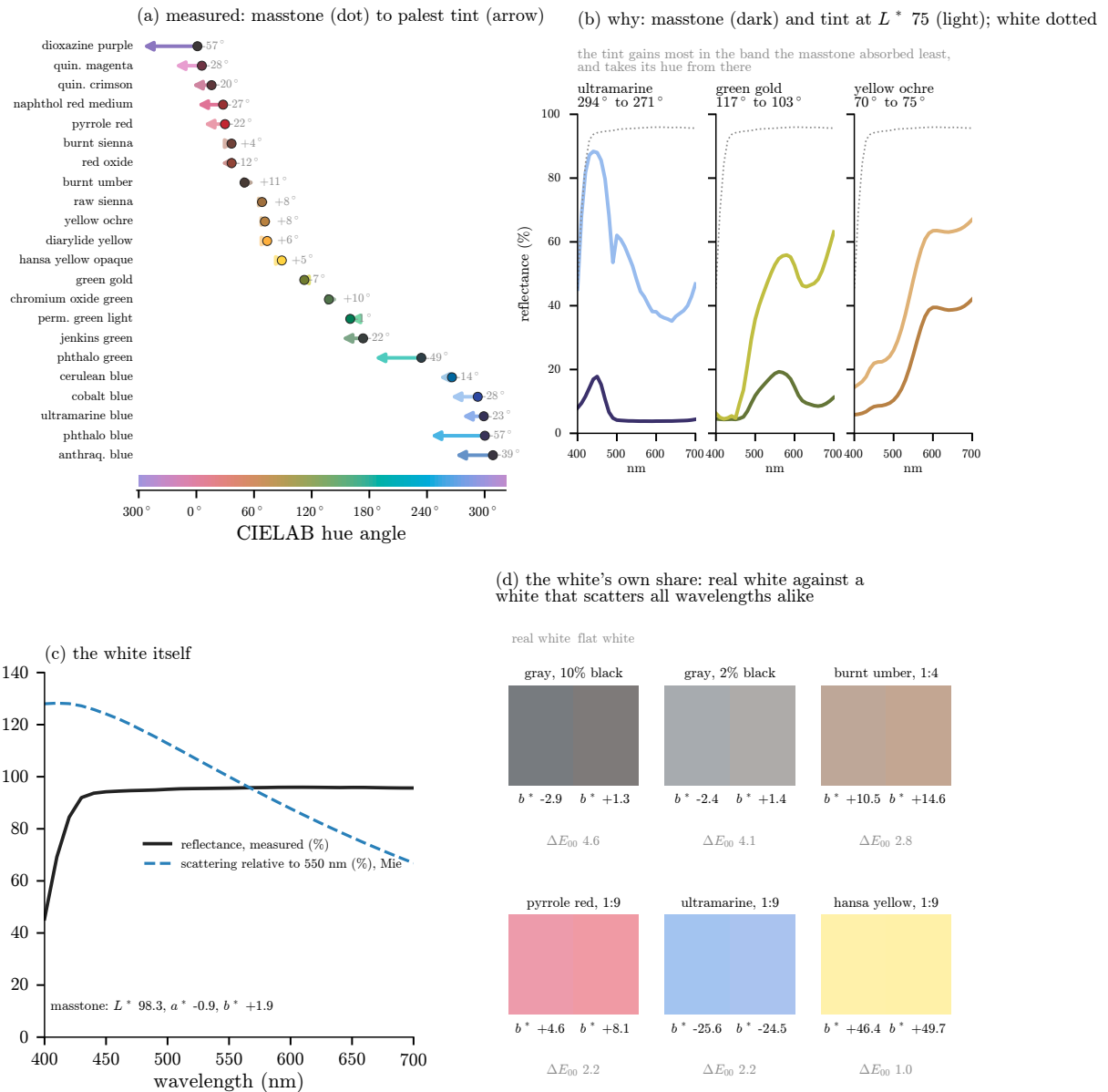


Figure 19: What white does to a hue. (a) Okumura's measured tint ladders [59]: for each paint, an arrow from the hue of the masstone to the hue of its palest tint, with the shift in degrees; hues above 320° are drawn below zero so that the reds are not split at the top of the circle. (b) The cause, for three paints: the measured masstone and the modeled tint at a lightness of 75, with the white dotted. The tint gains most where the masstone absorbed least. (c) The white itself: its measured reflectance [71], and how strongly its particles of rutile, the form of titanium dioxide in the paint, scatter each wavelength compared with green light at 550 nm, calculated from the physics of small particles. (d) The white's own share: six mixtures made with the real white and with an imaginary white of the same reflectance that scatters every wavelength equally, with the yellow-blue coordinate b^* of each and the color difference between the two.

Green gold is a mixture of yellows with a little phthalo green in it, enough in a thick layer to take out the red and make the color an olive green. It absorbs the blue very strongly and the red only about a tenth as much. In a tint the red opens first, and by half white the red is as bright as the green while the blue is still dark, so the paint has become a yellow. Yellow ochre reflects the red almost fully and the yellow nearly so, and absorbs the green much less than the blue. The green opens next, and the ochre's tint is a greener yellow than its masstone.

The weakest colors come back first because of the curve of Section 2.1. In a dark masstone, every color the paint absorbs strongly is close to black, however different their absorptions: a color absorbed ten times more is ten times darker, but both are near nothing. In a pale tint every color sits near the top of the curve, where a large difference in absorption becomes a much smaller difference in how far each color falls short of white. The tint squeezes the absorbed colors together, so the weakly absorbed ones gain on the strongly absorbed ones, and a pale tint shows the paint's own color blended with its next-weakest one, in proportions the masstone never showed. The eye then gives extra weight to the blue end: as with the reds, a little added violet moves a color further on the color map than the same amount of added green.

The rule needs some care when it is read off a masstone. Where all of a paint's absorbed colors sit on the surface floor of Section 2.2, as pyrrole red's do below 580 nm, the masstone cannot say which of them is weaker, and only a tint ladder can. The model takes that information from the ladders of the calibrated paints (Section 2.6), and the paints without ladders, the cadmiums and the cobalt greens among them, are left out of the model for that reason.

Read family by family, the rule gives back the painter's experience with the reasons attached. A red's next-weakest color is the violet, so reds turn pink. A blue's is the green side of its own peak, so blues turn toward cyan, and the phthalos, nearly black with a violet leak, swing furthest. A dark green such as phthalo green or jenkins green passes a narrow band of blue-green, and its tint fills in the green beside that band, so the blue masstone becomes a green tint; the ladder shows this, and the masstone alone, dark down to the surface floor on both sides of its band, cannot predict it. A yellow's next color is the blue-green side of the step where its reflectance rises, so yellows turn toward lemon. The earths reflect red fully, yellow nearly and green a little, so their tints gain green before blue and move toward yellow, and green gold's next color is the red, so it moves toward yellow too.

In the painter's words most of these shifts are coolings and a few are warmings. The saying that white cools holds for the reds, blues, violets, yellows and dark greens, fails for the earths and green gold, and has not been measured for the cadmiums. The direction cannot be read from a hue name, only from the spectrum or from a ladder.

The white's own share is small, and panels (c) and (d) measure it. Titanium white is very slightly yellow in the tube, because it absorbs a little of the violet [71, 25]. In a mixture it pushes the other way. Its particles scatter violet and blue light more strongly than red, and in a mixture the white's scattering is what sends the light back, so a colorant's absorption counts for less in the blue than in the red, and even a black that absorbs every color evenly gives a slightly bluish gray. Panel (d) makes six mixtures twice, once with the real white and once with an imaginary white of the same reflectance that scatters every color equally. The gray of ten percent carbon black is faintly blue with the real white and faintly yellow with the imaginary one, and tints of colored paints differ less. Okumura's measured gray of carbon black in white is indeed a faint blue [59], though blacks have undertones of their own as well, mars black giving warmer grays than carbon

black and the finest carbon blacks the bluest [8], and the tint ladders cannot separate the white's share of a bluish gray from the black's.

Either way the white's effect is small. It moves a red or a blue tint by three to six degrees of hue and a yellow not at all, while the pigments' own colors move tints by up to 57 degrees. The old description of titanium white as slightly yellow in the tube and mixing blue is true as far as it goes. What a painter sees when a red turns pink, a blue turns toward cyan or an ochre turns toward lemon is the pigment's next color coming through, and any white would show it.

3.8. The split-primary palette tested with measured paints. Many painting books teach a palette of six paints, a warm and a cool version of each primary: a lemon yellow and a deeper, more orange yellow, an orange-red and a cooler magenta-red, a violet-blue and a green-blue. The idea behind it is that no paint is a pure primary. Each one leans, or is biased, toward one of its neighbors on the color circle, the lemon toward green and the deep yellow toward orange. To mix the cleanest green, the rule says, take the yellow and the blue that both lean toward green; the yellow and the blue that lean away from it will give mud. The same goes for the oranges and the violets, the other two secondary colors. The palette and its rule are set out by Wilcox [75, 76] and taught, with variations, in many manuals [28]. MacEvoy and Briggs have both kept the palette while criticizing the explanation [48, 5].

Tested with the calibrated paints, the rule comes out partly right. With the palette's own six paints it gets the order right every time. With other paints from the same families it often does not, because a paint's lean is not what decides its mixtures. What decides them is how much light the two paints both reflect in the part of the spectrum the mixture needs, together with three properties the lean does not show: how dark each paint is, how strong it is, and how much of the mixture's scattering it supplies. A lean predicts mixtures only when the paints compared are alike in those three; in the palette's six, the lean and those three happen to point the same way.

The rule is easy to test with the model. Golden makes paints that fit the palette, and all six are among the calibrated paints: hansa yellow medium and diarylide yellow as the cool and warm yellows, pyrrole red and quinacridone magenta as the warm and cool reds, ultramarine blue and phthalo blue (green shade) as the warm and cool blues. For each secondary there are four ways to choose one paint from each of the two families it is mixed from. Each pair is mixed in every proportion, each mixture is lightened with white to the same lightness, and the one that lands on the chosen green, orange or violet is kept. Its chroma is the most vivid color that pair can make there. The targets, every chroma behind this section and the counts of the wider test below are in the appendix to this part (Section 3.12).

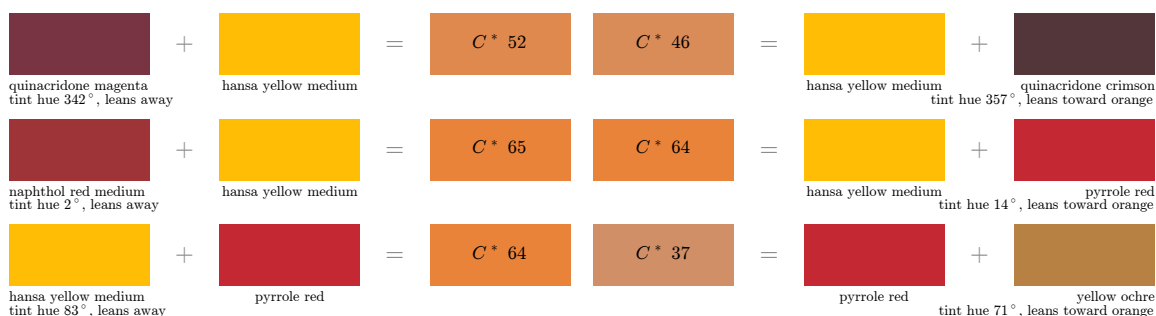
With these six, the two paints that lean toward a secondary make the most vivid one every time, and for greens the gap is large: hansa yellow medium with phthalo blue makes a green nearly four times as vivid as diarylide yellow with ultramarine, which is the mud the rule promises. The sizes of the gaps say more than the rule does, though. In the greens, changing the yellow makes at least as much difference as changing the blue. In the oranges, changing the yellow makes a little more difference than changing the red. In the violets the red decides almost everything: quinacridone magenta makes a vivid violet with either blue and pyrrole red a dull one with both, and phthalo blue, the rule's own example of a blue that cannot make a violet, does about as well as ultramarine. The oranges never turn to mud. Hansa yellow medium with quinacridone magenta, the pair that leans away, still reaches two thirds of the chroma of the best pair. The

Color Nerd channel tested the palette with real watercolors in the pigments of Wilcox’s own palette and found the greens and violets behaving as the rule predicts and the two oranges nearly alike [15]; the model puts the oranges further apart than that.

(a) greens at L^* 60 and hue 155°



(b) oranges at L^* 65 and hue 58°



(c) violets at L^* 45 and hue 315°

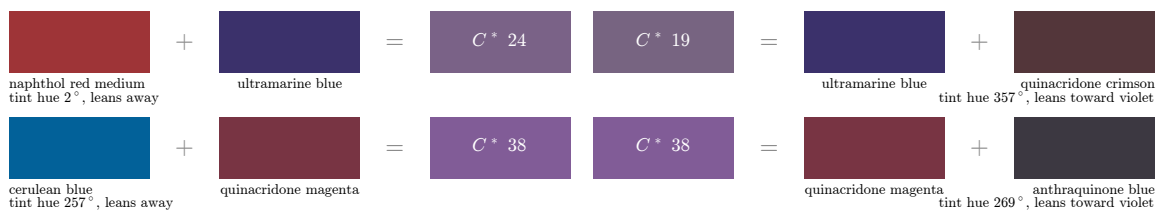


Figure 20: The split-primary rule tested with other paints from the same families. Each row compares two paints of one family, each mixed with the same partner. On the left are the paint that leans away from the secondary, its partner and their mixture; on the right are the mixture made by the paint that leans toward the secondary, its partner and that paint, so that the two mixtures sit side by side. The label under each paint gives its lean, the hue of its tint, relative to the other paint in its row. Each mixture is the most vivid one the pair can make at the target hue and lightness, and its chroma is written on it. In three rows the paint that leans away wins, by 5 to 27 units; in the other three the two mixtures are within a unit of each other, where the rule predicts a clear difference.

The trouble is that the six are chosen to agree with the rule. In each family the paint that leans toward a secondary also tends to have one of those three properties on its side, so its lean and its other properties point the same way, and a test with these six cannot tell which of them does the work. To pull them apart, the lean needs a number. The natural reading of the rule’s words is the hue of the paint’s tint, the paint mixed with white to a middle lightness, read as an angle round the color circle of Section 1.7. On that circle zero degrees is a pinkish red. Quinacridone

magenta's tint lies on the violet side of it, so the magenta leans toward violet; pyrrole red's lies well on the orange side, so it leans toward orange. A lean is also relative. Quinacridone crimson lies between quinacridone magenta and naphthol red, so it leans toward orange beside the magenta and toward violet beside the naphthol, and Figure 20 labels it each way in different rows.

With a number for the lean, the test can take every two paints of a family, mix each with the same partner, and ask whether the one that leans toward the secondary makes the more vivid mixture: two reds, each with the same yellow, for an orange, or two blues, each with the same yellow, for a green. Among the more vivid paints of each family the rule usually picks the better mixture or comes out even, and the paint that leans away wins only a few times. The earths and Payne's gray do worse. They lean mostly by being dark and dull, and they go against the rule about half the time. Figure 20 collects six cases: three where the paint that leans away makes the more vivid mixture, and three where the rule predicts a clear difference and the two mixtures come out the same.

Quinacridone crimson leans further toward orange than quinacridone magenta does, yet with hansa yellow medium the crimson makes the duller orange. An orange at this lightness is mostly yellow, and the red's job is to take out the yellow's reflection of green without darkening its orange and red. The two quinacridones absorb green equally well. They differ at the two ends of the spectrum. The crimson leans toward orange because it reflects a little less violet than the magenta, but it also reflects only a third as much red, and red light is what an orange needs. Its mixture comes out darker, needs more white to reach the target lightness, and loses chroma to the white.

Red oxide, which the wider test includes though the figure does not, is the most orange-leaning of the reds with any real color, and it makes a duller orange still, for a different reason: it is opaque. Section 3.2 showed that each paint in a mixture counts, color by color, in proportion to its share of the mixture's scattering. Red oxide does nearly all of the scattering in the red and most of it in the orange, so the orange and red light that comes back from the mixture is mostly red oxide's own, and red oxide's own is dull. Naphthol red medium and pyrrole red, two vivid reds whose tints lean quite differently, make the same orange. So little of either is needed that its lean hardly enters, and the two absorb green about equally.

Yellow ochre goes wrong through darkness. It leans as far toward orange as diarylide yellow, but with pyrrole red it makes an orange about half as vivid, duller even than hansa yellow medium's. Ochre leans toward orange because it is dark: it reflects only about half as much orange and red light as hansa yellow medium. Its mixture with the red is too dark for the target and needs white, which costs chroma, while the diarylide mixture needs none. The ochre's lean is not even a fixed property of the tube. Its deeper tints lean toward orange and its pale ones toward lemon, the hue shift with white of Section 3.7 in another guise.

For violets the reds go wrong in the opposite direction. Quinacridone crimson leans further toward violet than naphthol red medium, yet with ultramarine it makes the duller violet, and it does the same with cobalt blue. A violet needs the red paint's red light as much as the blue paint's blue, because a mixture keeps only the light that both of its paints reflect. The crimson reflects no more violet than the naphthol does. Its tint looks cooler because it absorbs more of the orange, and absorbing more of the orange and the red also makes it the darker paint. A red leans toward violet by absorbing orange, and the more it absorbs, the darker and duller the

violet it makes. Quinacridone magenta, which really does reflect some violet light, makes the most vivid violet of the four reds.

Among the blues, cerulean, which leans toward green, makes a green with hansa yellow medium barely more vivid than ultramarine's, though ultramarine leans toward violet. The lean is true to the curve here, since cerulean does reflect more green light. But cerulean is a grayish paint, and the mixture that reaches the target green is mostly cerulean, so it can be little more vivid than the cerulean itself. Phthalo blue makes a green far more vivid than either because it is so strong. A small amount is enough to take out the yellow's red, that small amount does hardly any of the scattering, and the green that comes back is mostly the hansa yellow's own.

In a violet the blue's lean hardly matters. Cerulean and anthraquinone blue, one leaning toward green and the other toward violet, make the same violet with quinacridone magenta, and phthalo blue and ultramarine come close to it. The violet is about nine parts in ten magenta, and the blue's only job is to take out the magenta's red, which every one of these blues can do.

Among the more vivid blues the rule's order does hold for greens. Apart from ultramarine, which beats cobalt blue by three units, no blue that leans further toward violet makes a better middle green than one that leans further toward green, and the yellows make greens in the order of their lean, from green gold, the most vivid, through hansa yellow medium and diarylide yellow down to the earth yellows. A yellow's reflectance curve is a single step, low at the violet end and high at the red end, and where the step falls sets both its hue and how much green light it reflects, so for a yellow the lean reads the curve directly.

A lean is one number read off a curve, and a mixture depends on the whole of both curves: in each part of the spectrum it is bright only if both paints are at least partly bright there and neither has a large say through its opacity. The Color Nerd channel gives painters a related rule of thumb: mixtures across the circle bend toward green, because the middle of the spectrum is where the eye is most sensitive and where the tails of most pigments' curves overlap, so the greens a yellow and a blue can make depend on how much of the middle each one reflects [15, 16].

3.9. A gallery of mixtures around the circle. The rest of this part is mostly pictures. Fourteen calibrated paints spaced around the hue circle, opaque and transparent together, are mixed in every pair. Sixteen pairs are followed from one paint to the other in steps of ten percent. And twelve paints are each tried against all the others to find the ones that mix them to gray. The pictures show the lessons of the earlier sections in a form a painter can consult at the palette, and they add a few of their own.

The first two pictures are grids (Figures 21 and 22). The fourteen paints run along both edges in order of hue, from hansa yellow medium through the reds, violets and blues to the greens, and each cell holds the mixture of the paint in its row with the paint in its column, with its chroma and hue. In the first grid the cells above the diagonal are half of each paint by weight, and the cells below are the same mixtures with two parts of white. The white is where most of the differences show. Many of the half-and-half mixtures are so dark that they look alike, and their colors come out only in a tint, for the reason Section 3.4 gave.

Mixed by weight, the strong transparent paints take over whatever they are in. Half and half with diarylide yellow, phthalo blue gives a dark green and dioxazine a brown-gray. The second grid corrects for this. There each pair is mixed in the proportion at which the mixture is as different from one parent as from the other, the point where neither paint has won, and the

above the diagonal: one part of each by weight; numbers are C^* and hue

below the diagonal: the same with two parts titanium white; (o) opaque, (so) semi-opaque, (st) semi-transparent, (t) transparent

	hansa yellow med.	diarylide yellow	burnt sienna	pyrrole red	naphthol red med.	quin. magenta	dioxazine purple	ultramarine	cobalt blue	cerulean blue	phthalo blue	phthalo green	chromium oxide	green gold
hansa yellow med. (st)	96 83	92 73	36 64	69 33	55 33	47 33	7 85	24 133	29 123	33 128	14 156	31 150	43 124	60 98
diarylide yellow (so)	77 78	90 72	45 60	68 33	60 31	55 32	8 42	21 111	30 87	30 86	11 152	27 139	37 103	67 82
burnt sienna (o)	39 75	46 67	22 38	52 28	31 30	21 22	4 8	3 106	6 5	5 359	6 283	4 205	14 98	21 64
pyrrole red (so)	51 33	56 34	40 17	69 30	62 29	60 27	19 24	22 27	36 21	38 20	8 4	10 11	32 28	56 30
naphthol red med. (so)	51 24	55 28	41 8	53 13	49 28	43 25	5 44	6 54	13 20	16 14	2 287	0 127	16 30	31 34
quin. magenta (t)	41 30	48 34	33 358	49 7	52 1	30 11	4 330	6 295	20 311	21 313	11 289	4 249	9 6	14 43
dioxazine purple (t)	7 333	10 20	25 308	24 327	29 321	43 310	3 352	4 315	17 307	19 305	10 302	4 297	6 313	3 85
ultramarine (st)	31 140	26 110	8 256	17 337	25 328	39 306	47 301	29 294	53 301	43 293	23 293	7 228	13 166	16 151
cobalt blue (st)	36 121	35 90	4 359	26 358	32 347	40 319	46 303	44 280	57 294	44 280	34 293	13 225	13 162	21 151
cerulean blue (so)	38 122	35 89	5 2	28 359	34 349	39 323	45 303	39 274	32 263	37 267	33 285	20 206	16 161	28 152
phthalo blue (t)	37 173	20 161	24 236	17 270	23 289	35 282	42 290	44 266	44 257	42 253	24 298	10 278	12 202	10 178
phthalo green (t)	55 154	37 139	24 180	6 248	10 293	14 247	22 275	32 201	40 192	42 189	38 211	9 227	26 161	21 165
chromium oxide (o)	41 121	38 101	11 95	23 12	28 356	22 337	26 303	14 209	11 181	13 174	26 216	38 169	27 139	38 129
green gold (t)	71 100	71 85	41 84	45 41	45 35	35 48	5 95	38 140	42 126	43 127	45 170	58 156	48 121	38 117

Figure 21: Fourteen paints around the hue circle. Above the diagonal every pair is mixed half-and-half by weight; below it the same mixtures have two parts of titanium white added. The diagonal holds the paints themselves, and each cell gives chroma and hue. Opacity ratings follow Golden's chart [25].

above the diagonal: the proportion (printed, earlier paint first, by weight) at which the mixture is equally far from both parents
below the diagonal: the same mixture with an equal weight of white; • marks a pair whose tinted mixing line passes within $C^* 8$ of gray

	hansa yellow med.	diarylide yellow	burnt sienna	pyrrole red	naphthol red med.	quin. magenta	dioxazine purple	ultramarine	cobalt blue	cerulean blue	phthalo blue	phthalo green	chromium oxide	green gold
hansa yellow med. (st)	96 83	94 77 87:13	51 74 78:22	74 58 96:3	72 57 97:3	64 55 92:8	49 93 96:3 •	38 124 76:24	27 124 47:53	34 128 51:49	47 132 94:6	61 129 92:8	65 106 92:8	63 97 56:44
diarylide yellow (so)	77 85 87:13	90 72	50 62 58:42	72 50 91:9	70 48 92:8	63 46 80:20	36 73 92:8	25 106 57:42	17 90 30:70 •	20 92 33:67 •	27 117 85:15	43 111 87:13	48 91 76:24	56 87 26:74
burnt sienna (o)	53 84 78:22	50 69 58:42	22 38	43 28 72:28	34 29 36:64	21 21 45:55	10 35 90:10	2 132 42:58 •	10 297 24:76 •	7 287 30:70 •	1 49 86:15 •	6 66 90:11 •	14 90 55:44	22 84 27:73
pyrrole red (so)	60 76 96:3	63 58 91:9	32 19 72:28	69 30	59 28 35:65	49 22 16:84	27 24 70:30	17 28 39:61	20 351 17:83	19 326 12:88	21 23 82:18	12 15 56:44 •	13 67 16:84 •	25 66 5:95
naphthol red med. (so)	59 73 97:3	62 55 92:8	44 8 36:64	53 12 35:65	49 28	38 22 26:74	19 33 92:8	8 48 58:42	10 331 23:77	15 312 16:84	10 38 90:10	8 41 84:16	8 74 15:85 •	19 71 7:93
quin. magenta (t)	54 73 92:8	56 53 80:20	35 356 45:55	49 355 16:84	51 355 26:74	30 11	13 359 98:2	8 346 92:8	21 309 46:54	29 302 24:76	10 351 98:2	6 347 96:4	5 77 26:74 •	13 76 19:81
dioxazine purple (t)	47 96 96:3 •	41 77 92:8	12 7 90:10	24 346 70:30	37 357 92:8	49 337 98:2	3 352	12 292 10:90	26 305 30:70	35 299 14:86	11 301 42:58	6 369 10:90	7 136 12:88 •	13 126 7:93 •
ultramarine (st)	44 122 76:24	30 105 57:42	11 256 42:58 •	15 318 39:61	26 336 58:42	44 331 92:8	47 291 10:90	29 294	50 301 59:41	41 286 24:76	23 292 70:30	12 274 96:4	8 208 74:26	7 167 92:8
cobalt blue (st)	35 123 47:53	23 96 30:70 •	10 268 24:76 •	16 308 17:83	27 324 23:77	39 318 46:54	45 301 30:70	45 281 59:41	57 294	45 282 56:44	37 292 64:36	23 254 90:11	9 215 70:30	15 197 92:8
cerulean blue (so)	38 122 51:49	25 95 33:67 •	7 273 30:70 •	16 295 12:88	26 318 16:84	32 306 24:76	38 294 14:86	34 267 24:76	33 264 56:44	37 267	35 282 62:38	27 224 87:13	13 205 75:25	26 187 93:7
phthalo blue (t)	53 129 94:6	33 115 85:15	7 217 86:15 •	15 338 82:18	27 345 90:10	45 333 98:2	42 288 42:58	44 271 70:30	43 257 64:36	41 251 62:38	24 298	11 279 51:49	11 212 59:44	11 176 46:54
phthalo green (t)	63 125 92:8	47 108 87:13	7 102 90:11 •	5 285 56:44 •	23 348 84:16	38 332 96:4	28 202 10:90	36 271 96:4	29 226 90:11	31 212 87:13	38 212 51:49	9 227	20 172 74:26	27 159 31:68
chromium oxide (o)	63 105 92:8	50 90 76:24	11 86 55:44	6 65 16:84 •	8 4 15:85 •	8 343 26:74 •	3 235 12:88 •	20 250 74:26	11 221 70:30	13 213 75:25	27 221 55:44	42 175 74:26	27 139	38 130 52:48
green gold (t)	72 99 56:44	68 90 26:74	48 92 27:73	49 91 5:95	45 79 7:93	40 77 19:81	38 105 7:93 •	20 202 92:8	23 172 92:8	25 173 93:7	45 167 46:54	59 148 31:68	47 122 52:48	38 117

Figure 22: The same fourteen paints, each pair mixed in the proportion at which the mixture is as different from one parent as from the other, so that neither has won (above the diagonal, with the proportion printed, earlier paint first), and the same mixtures with an equal weight of white (below). A dot marks a pair whose tinted mixing line passes close to gray, within a chroma of 8.

proportion is printed in the cell. It runs from about equal for paints of similar strength, such as hansa yellow medium and cerulean, to almost all quinacridone magenta against a trace of phthalo blue. The proportions measure tinting strength, how far a gram of each paint goes in a mixture (Section 3.1). A painter who mixes by eye will use the phthalos and dioxazine in traces and cobalt blue and cerulean by the spoonful.

The lower triangles show what white does. In the hansa yellow medium row the greens gain from it, a few units of chroma with ultramarine, cobalt or cerulean and more than twenty with the two phthalos. Half and half with phthalo blue, the yellow makes a dark green, and white more than doubles its chroma, giving back light the dark blue would have absorbed. The red-oranges in the same row lose chroma with white. The quinacridone magenta and dioxazine rows are dark most of the way across in masstone, and they show their colors only in a tint, where some of their mixtures with the blues become clear violets and violet-blues.

A dot in the second grid marks a pair whose mixing line, with white, passes close to gray. The dots fall on pairs from opposite sides of the circle: burnt sienna with each of the four blues and with phthalo green, the reds and magenta with chromium oxide, hansa yellow medium with dioxazine, diarylide yellow with cobalt blue or cerulean, among others. Pairs that balance near equal weights and never pass through gray, such as hansa yellow medium with cerulean, are the ones a painter can mix by eye without surprises.

Sixteen mixing lines, in Figures 23 and 24, follow pairs from one paint to the other, each in masstone and with white; Section 3.12 gives sample values from the grids and along several of the lines. Pairs of neighbors stay vivid; in masstone a dark transparent paint can take over a line, as phthalo green does when it goes into cerulean. Hansa yellow medium to diarylide yellow hardly dips. Diarylide yellow to pyrrole red drops by about a fifth at the first step and then holds. With white the hue walks evenly round the circle, from pyrrole red through the pinks to quinacridone magenta, or from dioxazine through the violet-blues to ultramarine. Pairs from across the circle dive toward gray instead. Hansa yellow medium to ultramarine passes through a run of greens, each duller than the last. Naphthol red medium with phthalo blue is close to gray by 30 percent blue. Burnt sienna with ultramarine, the painter's classic gray, is nearly gray by the same point, and with white it runs from a warm gray to a cool one with every neutral in between. Yellow ochre with dioxazine gives a long run of browns and gray-violets.

These are the lines a painter uses for neutrals, and the figure shows where on each line the neutral sits. Two paints from opposite sides of the circle reflect different parts of the spectrum, so each absorbs most of what the other reflects. Somewhere along the line their reflections stop overlapping, no part of the spectrum comes back much brighter than any other, and the mixture is gray.

The word complement means two different things. To the eye, the complement of a color is the hue directly across the color circle, the one the opponent channels of Section 1.3 treat as its opposite. To a painter it is the paint that mixes with it to gray. The search in Figure 25 finds the second kind. Each of twelve paints is lightened to a middle lightness, every other colored paint among the calibrated ones is tried against it in every proportion, and the partners that bring the mixture close to gray are marked on a hue scale, along with a tick at the hue exactly opposite. This test is stricter than the dots of the second grid, so its lists differ a little from the grid's. A dot marks any pair among the fourteen whose tinted line comes within a chroma of 8 of gray; the search asks for a chroma below 4 at a fixed lightness and tries every colored calibrated

neighbours round the circle, in steps of 10 percent by weight; the number in each swatch is its chroma C^*

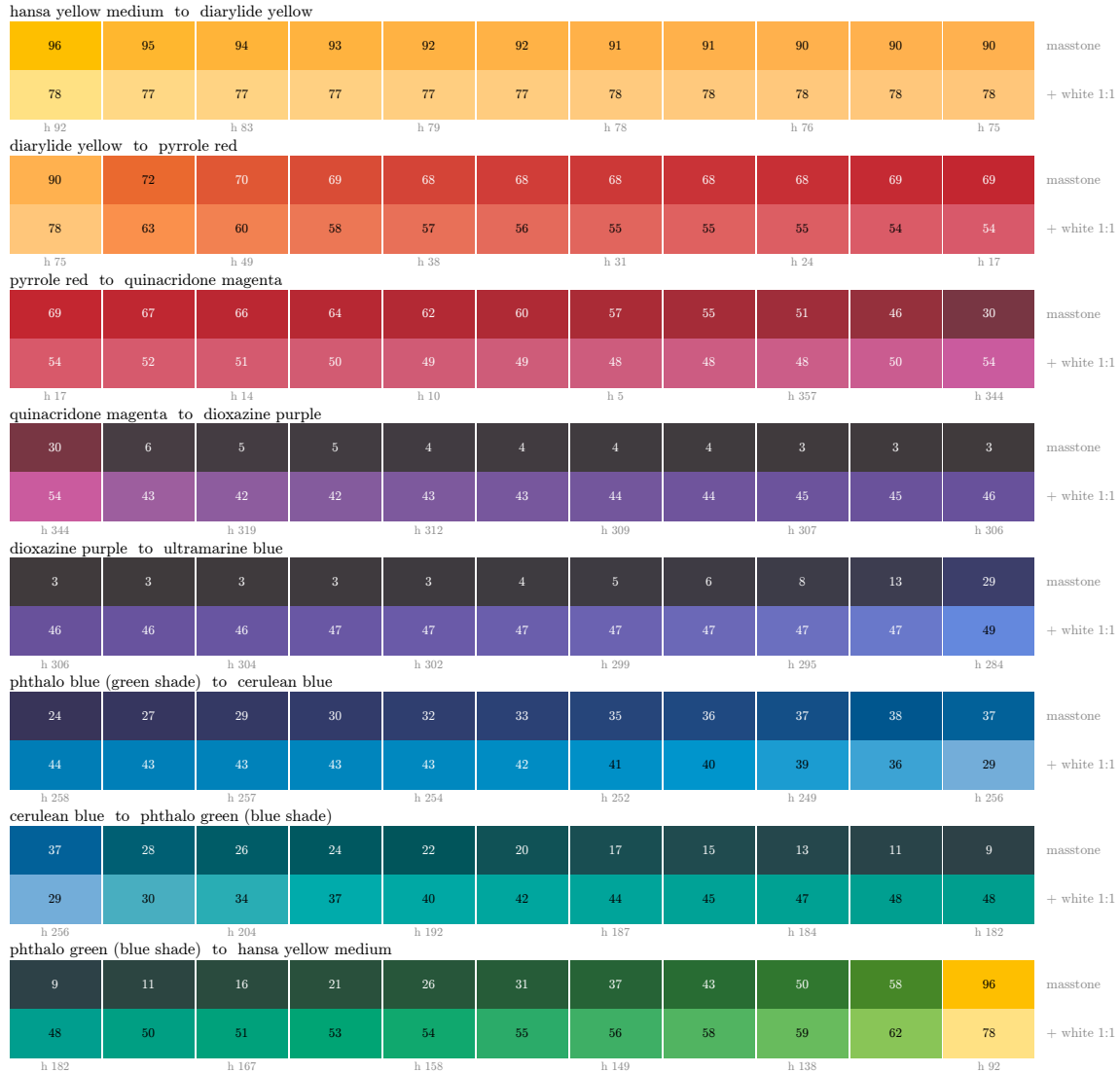


Figure 23: Eight pairs of neighbors going round the hue circle, mixed in steps of ten percent by weight. The upper row of each pair is the mixture; the lower row is the same mixture with an equal weight of titanium white, with its hue under every other step. The number in each swatch is its chroma.

pairs from across the circle, in steps of 10 percent by weight; the number in each swatch is its chroma C^*



Figure 24: Eight pairs from across the hue circle, mixed in steps of ten percent by weight, in masstone and with an equal weight of white, as in Figure 23. The pairs pass through gray where the two reflectances no longer overlap.

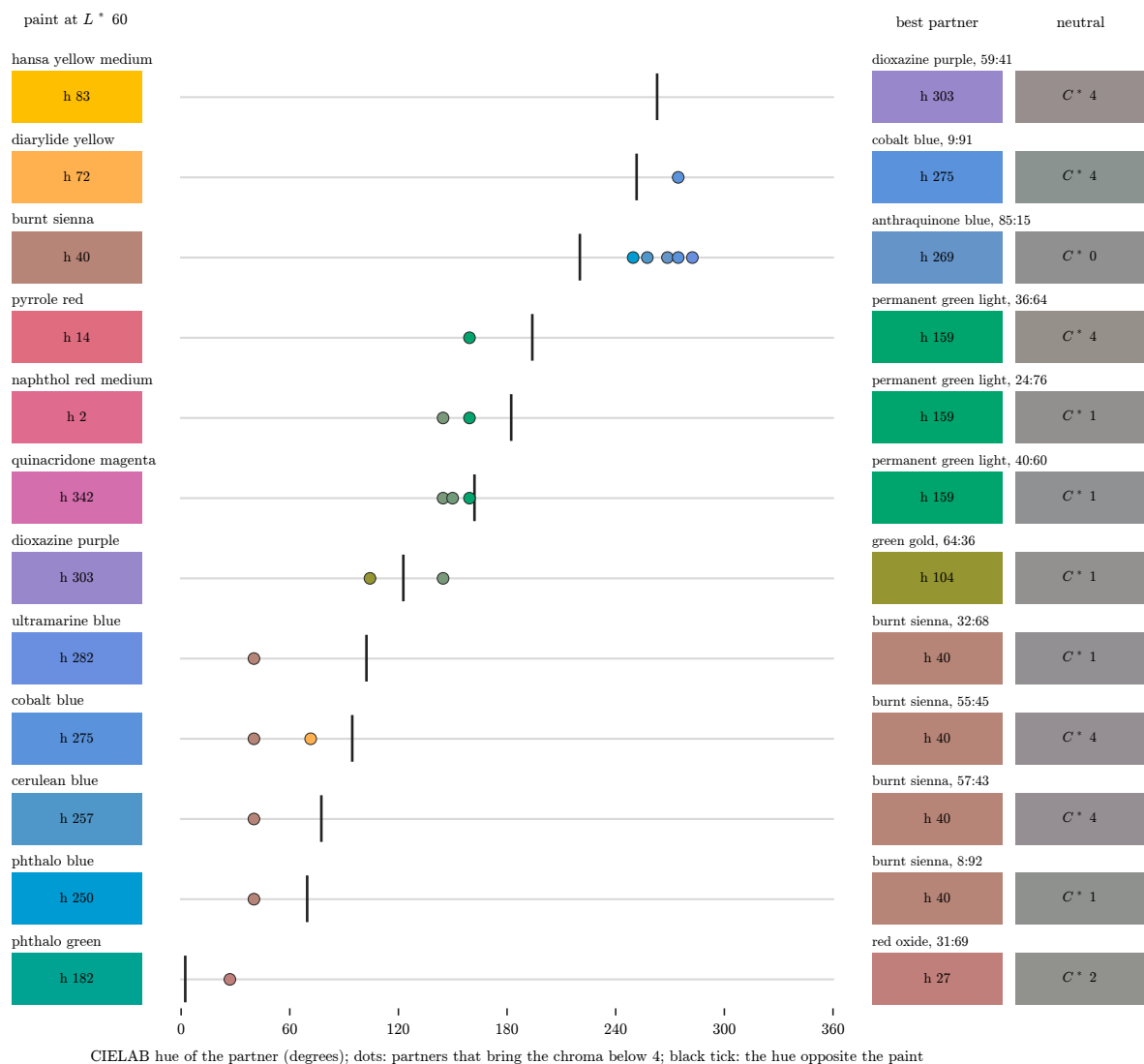


Figure 25: Mixing complements. Each of twelve paints, lightened with white to a middle lightness ($L^* = 60$), was mixed in every proportion with every other colored calibrated paint at the same lightness. The dots on the hue scale mark each partner that brought the mixture nearly to gray, below a chroma of 4, and the black tick marks the hue exactly opposite the paint's tint. On the right are the partner that came closest to gray, the neutral it made and the proportion.

paint as a partner.

The two kinds rarely coincide. Ultramarine's visual opposite is a yellow, but the one paint that neutralizes it is burnt sienna, an orange-brown, at about one part blue to two of sienna. The other blues go the same way, cobalt, cerulean and phthalo blue all neutralized best by burnt sienna, and in return burnt sienna is neutralized by five of the blues. Diarylide yellow's opposite is a middle blue, but its only neutralizer is cobalt blue, from the violet end of the blues, and it takes far more of the blue than of the yellow. No calibrated paint brings hansa yellow medium below a chroma of 4, though dioxazine comes close. Of these twelve, only quinacridone magenta and dioxazine, neutralized by greens close to their opposites, come near to agreeing with the eye. The misses have a direction. The blues' partners lie toward red from the visual opposite, the yellows' toward violet and the vivid reds' toward yellow, and phthalo green's partner, red oxide, lies toward orange.

The visual opposite comes from the eye's color channels, while a mixing complement comes from two reflectance curves: to leave a gray, the partner must absorb where the paint reflects and reflect where it absorbs, with matching strength. A yellow reflects everything from green to red, roughly from 500 nanometers up, so its partner must absorb all of that and reflect only violet and blue. Most blue pigments do not. Cobalt and ultramarine reflect some green along with their blue, and phthalo blue a great deal of it, so a yellow mixed with a blue usually keeps the green they share and makes a green. Dioxazine reflects violet and blue and absorbs the rest, and it comes closest to neutralizing hansa yellow. Diarylide yellow, the more orange of the two yellows, has less green in its curve, and cobalt blue can neutralize it given enough. A blue, in turn, reflects from violet to blue-green with a small tail into the red. A yellow reflects the green part of that and so leaves a green. Burnt sienna absorbs all of it, and its own reflection in the red matches the blue's tail. So a blue's mixing complement is an orange-brown, a yellow's is a violet or a violet-blue, and a green's is a red-orange or a magenta-red. Magenta and green come near to agreeing with the eye because magenta reflects both ends of the spectrum and green the middle, so for this pair the halves of the spectrum line up with the eye's opposites. Part 4 takes this to the color wheel, whose opposite pairs turn out to be fair mixing complements with these paints even though the hue the eye sees as opposite often belongs to another paint.

3.10. Darkening with black and with the complement. Black, the manuals say, deadens a color, while a complement or an earth darkens it and keeps it alive. The model can test this directly. Take a paint, darken it to a chosen lightness in three ways, with carbon black, with a complement that mixes with it to near gray, and with burnt umber, and compare the results.

The chroma comes out about the same whichever way the paint is darkened. Pyrrole red taken down to a fairly dark lightness ends at the same chroma, within a unit, whether it is darkened with black, with permanent green light or with umber, all at the same hue. Hansa yellow medium ends at the same chroma all three ways, and diarylide yellow and permanent green light come close to that; the recipes are written out in Section 3.12. Adding white back to the darkened reds does not separate them either. In Figure 26(a) the three darkening lines of each paint lie close together. The one small exception is umber with the yellows, which keeps a few more units of chroma because umber is itself a dark yellow-brown.

The hue does change. Black and the complement both turn the yellows toward green, by 8 to 14 degrees, while umber holds them within a few degrees of where they were; panel (b) of the figure shows the swatches side by side. The manuals are right that black changes a color, but

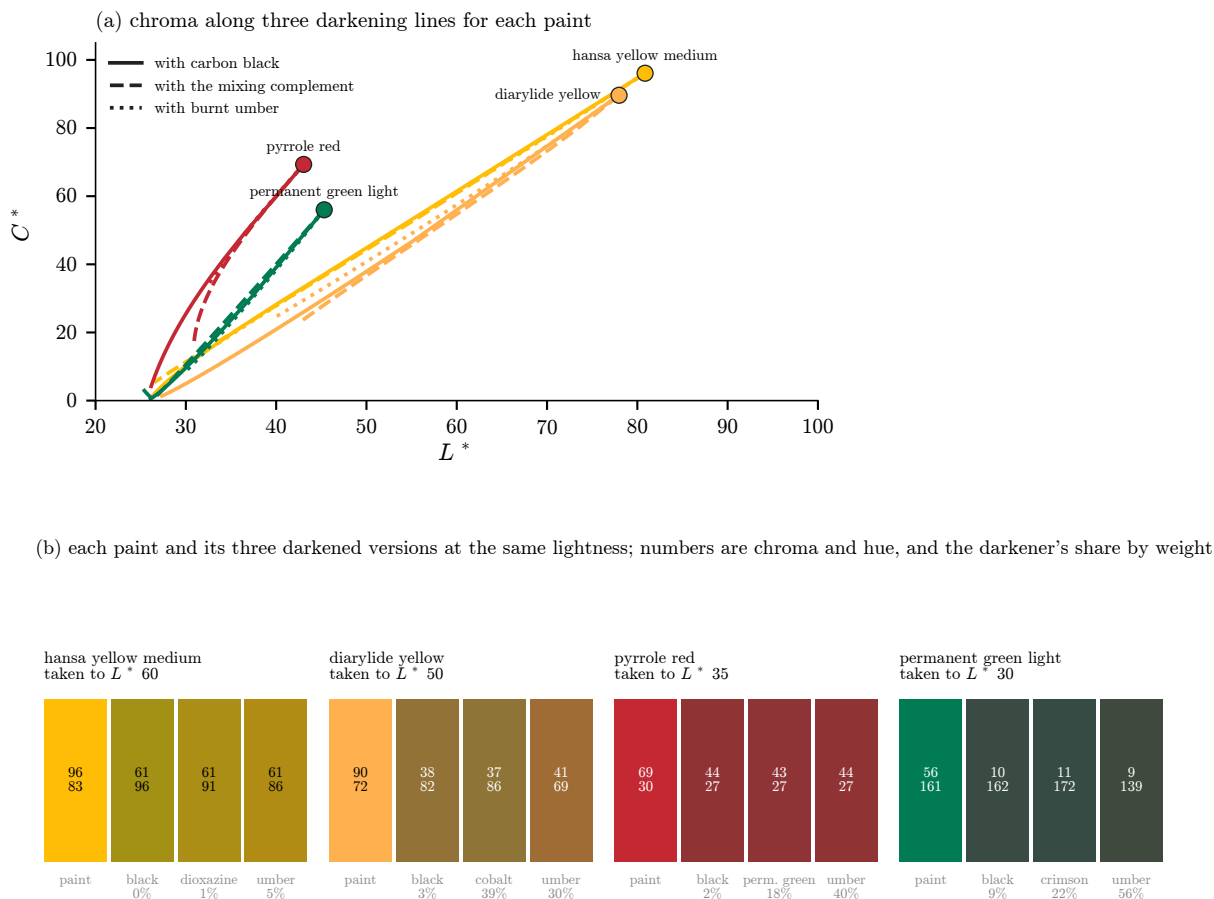


Figure 26: Darkening with black and with a complement. (a) Chroma against lightness as each of four paints is darkened with carbon black (solid), with a complement that mixes with it to near gray (dashed) and with burnt umber (dotted). The three lines of each paint nearly coincide. (b) Each paint and its three darkened versions at the same lightness, with chroma, hue and the darkener's share by weight.

the change is in hue: at any given lightness black leaves as much chroma as a complement or an earth would.

A colored paint reflects strongly in one part of the spectrum and weakly in the rest, and nearly all of its lightness comes from the bright part. Any darkener that brings it to a given lightness has therefore dimmed the bright part to about the same level. Chroma is the contrast between the bright part and the rest, and the rest was dark to begin with and can only get darker, so the chroma comes out about the same too. The three darkeners differ in which wavelengths they take the light from, and that decides the hue. Carbon black, as the model has it, absorbs more at the red end than at the blue, so it takes more red than blue from a yellow and turns it toward green. That is part of the olive that yellow and black are known to make; the rest is the eye's habit of seeing any dark yellow as olive (Section 4.2). Umber absorbs most at the blue end and holds a yellow nearest its own hue.

The model's black comes from Okumura's ladder of carbon black in white, and that ladder cannot fully separate a black that absorbs more red from a white that returns more blue (Section 3.7), so the size of black's turn toward green is less certain than the rest. The equal chroma does not depend on it, since it holds for three darkeners that absorb and scatter very differently. There are still good reasons to prefer a complement or an earth to black. The hue shift of black is usually unwanted, and umber avoids it, though a complement only sometimes does. And every black has an undertone of its own, bluish for carbon black and warmer for mars black, which shows in the mixture.

3.11. Matching colors by computer. The paint industry has matched colors by computer since the 1960s, with the same two-constant law used in this paper. A manufacturer measures each of its pigments in masstone and in tints with white, works out each one's absorption and scattering at every wavelength, and stores them; Section 3.12 describes how. To match a target, the software searches for the amounts of three or four pigments that make the mixture's color equal the target's under a chosen illuminant, and reports how far the match drifts under other illuminants. A mixture made from different pigments than the target has a different reflectance curve, which makes it a metamer of the target (Section 1.4): a match under one light that can come apart under another. In industry the first batch is then measured and the recipe corrected, and after one or two corrections a match within a unit of color difference is routine [39, 3].

Four patches of the ColorChecker, a chart of colored squares whose reflectances were measured for testing color reproduction, make the test in Figure 27. Each patch is matched with three Golden paints and white under daylight. For the patch called dark skin, more than a hundred different sets of three paints give a match within one unit, about the smallest difference a careful observer can see. They are far from equivalent. The recipe whose reflectance curve lies closest to the target's is mostly burnt sienna, with a little hansa yellow, white and carbon black, and under a tungsten illuminant or the narrow-band fluorescent F11 it stays within half a unit of the target. The recipe whose curve lies farthest away, cobalt blue with hansa yellow and pyrrole red, matches just as well in daylight but drifts by 3.5 units under tungsten, which anyone would see. This drift under a second illuminant is called the index of metamerism [11], and among recipes that are all perfect in daylight it ranges from invisible to obvious.

The foliage and blue sky patches agree: the recipe nearest the target's curve drifts less than the one farthest from it. The orange patch is the exception. Its closest recipe, diarylide yellow with a little red oxide and pyrrole red, holds up better under tungsten than hansa yellow with quinacridone magenta, whose curve is farther from the target's, but worse under F11, the illuminant whose light comes in three narrow bands.

A painter who cannot compute can still use the result. A color matched with pigments like the target's, which for a skin tone means an earth, holds up better when the light changes than one matched with unrelated pigments, though not under every light, as the orange patch shows.

3.12. Appendix: the mathematics.

Mixing lines and the two-constant law (Section 3.1). The law is Duncan's extension of the Kubelka–Munk law to mixtures [22], already used in Section 2.6. Each paint i contributes absorption $K_i(\lambda)$ and scattering $S_i(\lambda)$ per unit weight, and in a mixture with weight fractions c_i

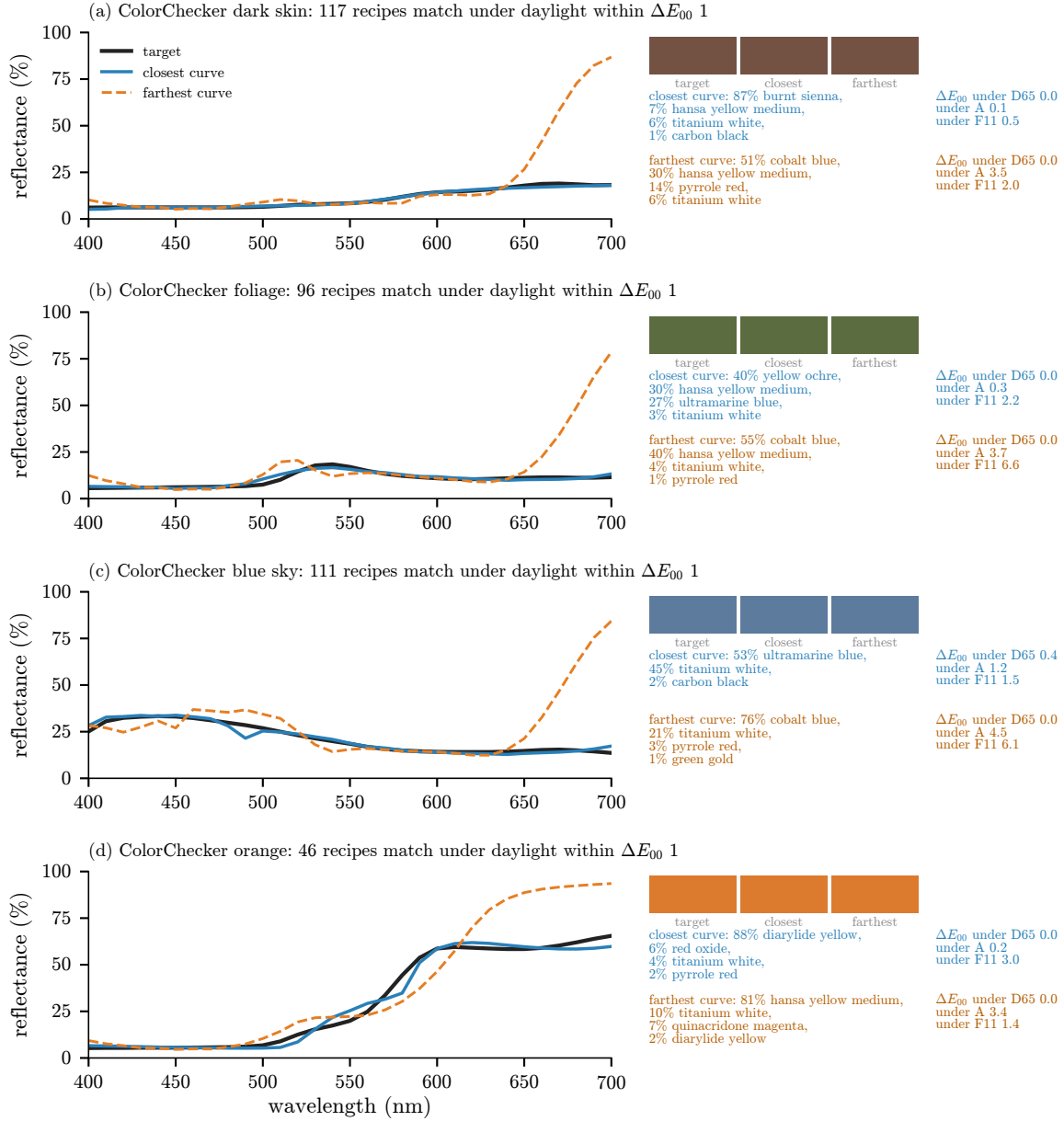


Figure 27: Matching by computer. Four ColorChecker patches matched under daylight with three Golden paints and white. For each patch, of all the recipes that match within one unit of color difference under daylight (D65), the one whose reflectance curve lies closest to the target's and the one whose curve lies farthest from it, with their color differences from the target under daylight, under a tungsten illuminant (A) and under the fluorescent illuminant F11.

both add:

$$\left(\frac{K}{S}\right)_{\text{mix}} = \frac{\sum_i c_i K_i}{\sum_i c_i S_i} = \sum_i w_i m_i, \quad m_i = \frac{K_i}{S_i}, \quad w_i = \frac{c_i S_i}{\sum_j c_j S_j}. \quad (20)$$

The second form is Principle 3.1: the mixture's K/S at each wavelength is a weighted average of the paints' masstone ratios m_i , and the weight w_i of a paint is its share of the mixture's scattering, its amount times its scattering over the total. The reflectance then follows from equation (8) and the surface from equation (9). A paint with little scattering has a small w_i , but in the bands it absorbs its m_i is in the tens or hundreds (Section 2.2), and what enters the sum is the product $w_i m_i = c_i K_i / \sum_j c_j S_j$, the paint's absorption per gram divided by the mixture's total scattering. That quotient is the tinting strength of the paint relative to the mixture it goes into. The squeeze at the light end has two parts. Near white the reflectance inside the paint is about $1 - \sqrt{2K/S}$, which falls fastest for the first trace of absorption, and lightness is close to a cube root of reflectance (Section 1.7); the two together make each equal step of lightness in Figure 13(c) need nearly twice the black of the step before, 0.14, 0.63, 1.8, 4.1, 8.9, 19 and 40 percent; the first eighth of the black does two thirds of the whole darkening, and the last half does less than a tenth of it. The same compression makes the lines lopsided. From hansa yellow medium, the first tenth of ultramarine moves the color 34 units of ΔE_{00} and the next eight tenths only 28 more; the first tenth of phthalo blue moves it 47 units, to a lightness of 41 and a chroma of 41, and the next eight tenths 32 more, with the half-and-half mixture at a lightness of 28 and a chroma of 14. Pyrrole red to ultramarine keeps a hue between 27° and 31° while its chroma falls from 69 to 22 at equal parts, and reaches a chroma of 2 at ninety percent blue; diarylide yellow to pyrrole red drops from the yellow's 90 to 72 at the first step and holds 68 to 70 after that.

The first sentence of Fact 3.2 is immediate from equation (20), since the weights are positive and add to one at each wavelength. The second is a line of algebra. For two paints, $(K/S)_{\text{mix}} = w m_1 + (1 - w) m_2$ with $w = c_1 S_1 / (c_1 S_1 + c_2 S_2)$ and $c_1 + c_2 = 1$. Replace paint 1 by a paint with the same m_1 and the scattering $k S_1$, k the same at every wavelength. Its weight is $c_1 k S_1 / (c_1 k S_1 + c_2 S_2)$, which is the old w at the proportion $c'_1 = k c_1 / (k c_1 + c_2)$, so every mixture of the new paint is a mixture of the old one in another proportion: the same colors, reached with a different amount of paint. The same algebra gives the more general result for a pair: if two paints' scattering spectra have the same shape, so that one is a constant multiple of the other, the set of colors the pair can make depends only on their two masstone K/S spectra, and their scattering strengths decide only how much of each paint by weight lands at each point of the line. For then S_1/S_2 is the same at every wavelength, w is one number for the whole spectrum, and as c_1 runs from 0 to 1 it runs from 0 to 1 whatever the two strengths are, so the mixture's K/S spectrum runs over the same straight segment between m_1 and m_2 . When the shapes differ, w differs from band to band, the mixture's spectrum leaves the straight segment, and the colors change. The mixing lines of hansa yellow medium and phthalo blue computed with the phthalo's fitted shape and with a flat shape lie 11 units of ΔE_{00} apart on average and up to 20, measured from each point of one line to the nearest point of the other. The fitted shapes are the least certain part of the model (Section 2.6), so this result is best read as a rule for paints of similar make, while the first sentence of the Fact holds whatever the shapes.

Subtractive and additive (Section 3.2). Take a band of wavelengths where paint 2 absorbs strongly and paint 1 hardly at all, so that $m_1 \approx 0$. There equation (20) becomes

$$\left(\frac{K}{S}\right)_{\text{mix}} = m_2(1 - \sigma), \quad \sigma = \frac{c_1 S_1}{c_1 S_1 + c_2 S_2}, \quad (21)$$

where σ is the share of the mixture's scattering that paint 1 supplies; if a white is present, its scattering goes into the numerator of σ as well. At $\sigma = 0$ the band is exactly as dark as paint 2 alone and the mixing there is fully subtractive; as σ approaches 1 the band approaches its brightness in paint 1 alone and the mixing is additive; in between, paint 2's own ratio is diluted by the factor $1 - \sigma$. The additive share of a mixture, in the band one pigment absorbs, is the share of the scattering supplied by everything else. An opaque blue's band is easier to lift because its m_2 is moderate: cobalt blue reflects 12 percent at 660 nm inside the paint, which is $m_2 \approx 3$, while phthalo blue reflects 2 to 3 percent across most of the red, m_2 of 13 to 20, and under 2 percent at 600 nm, where the fitted m_2 is above 40. At $1 - \sigma = 0.1$ the cobalt's band is at $K/S = 0.3$ and reflects 47 percent; the phthalo's is at 1.3 to 2 and reflects 17 to 23, and where it was above 40 it is at 4 or more and reflects under 10. In the thought experiment of Figure 14(a), the imaginary blue's scattering is none, 3 and 30 percent of the white's, against about 23 percent for chromium oxide. With the dye the mixture reflects 4 percent above 600 nm, where the yellow alone reflects 85, and has a lightness of 28; as the blue's scattering rises to the white's, the blue alone pales to a lightness of 54, the fraction of the average's light kept in its absorbed band rises from 8 to 58 percent, the chroma passes through 2 when the blue scatters a tenth of what the white does, and the mixture ends as a violet of chroma 13. Among the real pairs of panel (c), hansa yellow medium with phthalo blue reflects 5.6 percent of the light where the average would reflect 31, and keeps 12 percent in the phthalo's band; diarylide yellow with cerulean blue reflects 16 against 32 and keeps 47. The other three pairs keep 17 against 61 (quinacridone magenta with phthalo green, pyrrole red with chromium oxide), 17 against 87 (quinacridone magenta with phthalo blue, pyrrole red with cerulean blue) and 15 against 36 (hansa yellow medium with phthalo green, diarylide yellow with chromium oxide), so the opaque versions come two and a half to five times closer to the average in that band. The fully subtractive case has an exact law of its own, the product of transmittances for filters or glazes in series, where by equation (7) the exponents add. Optical mixing is the average of the two reflectances: dots of hansa yellow medium and phthalo blue give a lightness of 63, a chroma of 55 and a hue of 79° , where the stirred mixture is at 28, 14 and 156° ; dots of hansa yellow medium and ultramarine give a chroma of 48 at 77° ; dots of pyrrole red and phthalo green give 36, 43 and 22° , where the stirred mixture has a chroma of 10.

Why reds turn pink (Section 3.3). With the white as the partner, equation (21) applies band by band. In the red band, where the paint's m is near zero, the tint stays at the white's level: pyrrole red reflects 76 to 88 percent from 640 nm up in masstone and 82 to 88 at half white, against the white's 95. In the short-wave band, where m is 40 or more below 530 nm and 13 to 37 from there to the edge, the tint's K/S is $m(1 - \sigma)$ with σ the white's share of the scattering. Pyrrole red scatters about 7 percent of what the white does per gram at 550 nm and, in the fitted model, about a hundredth in the blue, so σ is close to one even at half white, and the band below 580 nm rises from the surface floor of 4 percent to 13 at half white and to 32 to 43 at one part red to nine of white. On the eye's side, equation (5) gives $b^* = 200 [f(Y/Y_n) - f(Z/Z_n)]$, and Z is the integral of the reflectance against $\bar{z}$, which lives entirely below 520 nm, so the added blue

raises Z a great deal and lowers b^* . The coordinate $a^* = 500 [f(X/X_n) - f(Y/Y_n)]$ falls much less, because the added green light raises X and Y together. The hue angle is $\arctan(b^*/a^*)$, and when b^* falls faster than a^* the hue rotates toward 0° and past it. In the model pyrrole red goes from 30° in masstone to 17° at half white and 4° at 98 percent white; naphthol red medium from 28° to 9° to -7° ; quinacridone magenta from 11° to -16° to -22° ; quinacridone crimson from 14° to -13° ; red oxide from 36° to 24° . Okumura measured pyrrole red going from 29.8° to 7.5° at ninety percent white, naphthol red medium from 27.8° to 0.8° at eighty percent, quinacridone magenta from 5.7° to 337° at ninety, quinacridone crimson from 15.8° to 355° at eighty and red oxide from 36.7° to 25.2° at eighty [59]. Red oxide's K/S is 5 to 10 at 540 to 560 nm, on its edge, against 14 across the blue, so white opens the edge nearly as fast as the blue.

Tints and the chroma peak (Section 3.4). For a paint with scattering $S_p(\lambda)$ and absorption $K_p(\lambda)$, tinted with a fraction $1 - t$ by weight of a white with scattering S_w and absorption K_w , the two-constant law of equation (20) gives

$$\left(\frac{K}{S}\right)_{\text{tint}} = \frac{tK_p(\lambda) + (1-t)K_w(\lambda)}{tS_p(\lambda) + (1-t)S_w(\lambda)} \approx \frac{t}{1-t} \frac{K_p(\lambda)}{S_w(\lambda)} + \frac{K_w(\lambda)}{S_w(\lambda)}. \quad (22)$$

The approximation holds where the white supplies most of the scattering, which for a transparent paint is its passed bands at every ratio beyond the first few percent of white, and its absorbed bands too unless its own scattering there is large. The white's own ratio K_w/S_w is a few ten-thousandths and matters only in the palest tints. A tint ladder is therefore a one-parameter family: the paint's absorption spectrum per gram, divided by the white's scattering, multiplied by the single number $u = t/(1-t)$, which falls from a large value toward zero as white is added.

Write g_{pass} and g_{abs} for K_p/S_w in a passed and an absorbed band and $R(x)$ for the Kubelka–Munk reflectance of equation (8) at $K/S = x$. The two bands reflect $R(u g_{\text{pass}})$ and $R(u g_{\text{abs}})$, and their difference is greatest where their rates of change with u match,

$$g_{\text{pass}} R'(u g_{\text{pass}}) = g_{\text{abs}} R'(u g_{\text{abs}}). \quad (23)$$

Since R' is largest near $K/S = 0$ and falls as K/S grows, and g_{abs} is more than a hundred times g_{pass} for a dark transparent paint, the condition is met when the passed band has a K/S of a few thousandths, a reflectance above 90 percent, while the absorbed band is at a K/S of a few units, reflecting 10 to 15 percent. For quinacridone magenta, the masstone has $K/S = 16$ at 550 nm, reflecting 3 percent inside the paint, and $K/S = 0.11$ at 650 nm, reflecting 62 percent; the difference between the two is 0.59. At equal parts with white it is 0.74, and at two percent paint 0.21. The model's peak is at 34 percent white, where the passed band reflects 93 percent and the absorbed band 14. The lighter a paint's passed band in masstone, the larger the u , and so the less white, at which equation (23) is met, which is why ultramarine peaks at 12 percent white and the phthalos at about 50, and why hansa yellow medium, whose passed band already reflects 85 percent in masstone, has no peak. A glaze over a white ground scales its exponent at every wavelength by the amount of pigment the light crosses, by equation (7), so a glaze series is the same kind of one-parameter family and peaks in the same way.

Mixtures more chromatic than both parents (Section 3.5). With white the gains are measured: in Okumura's ladders dioxazine goes from a chroma of 3 in masstone to 46 in its best tint, phthalo green from 8 to 48, ultramarine from 25 to 61 and quinacridone magenta from 28

to 54, with the white at about 1 [59]. Between two colored paints, equation (20) works band by band. Write m_1 for the first paint's ratio in a band, m_2 for the partner's and w for the partner's weight, so that the mixture's ratio is $(1 - w)m_1 + wm_2$. A mixture can be purer than both parents only if, at the proportion in question, the leak bands move up the K/S curve by more than the main band does. In the main band m_1 is small and m_2 must be not much larger, so that the mean stays small; in the leak bands m_1 is moderate and m_2 must be very large, so that a small w pulls the mean far up the curve. Chromium oxide reflects 17 to 23 percent in its green band, 13 percent at 400 nm and 21 percent at 700 nm; phthalo green (blue shade) reflects about 5 percent at both ends and passes a narrow band near 500 nm. Ten percent of it takes the reflectance at 400 nm from 13 to 6 and at 700 nm from 21 to 5, while the peak of the green band falls only from 23 to 21, and the chroma rises from 27 to 31. Along the line the chroma peaks at 31 with 15 percent phthalo green, the hue moving from 139° to 149° , and chroma over lightness rises from the parents' 0.61 and 0.33 to 0.73. The second route has $m_2 < m_1$ in the main band, so that the mean falls there and the band climbs the steep part of the curve while the partner's absorption holds the other bands down: cerulean blue and ultramarine, at chromas of 37 and 29, give 43 at equal parts. That gain depends on ultramarine's fitted scattering shape. A flat shape fits its ladder about as well, at 1.85 units of ΔE_{00} against 1.80, and with it the gain falls to under one unit. White is the limiting case of the second route, with no bands of its own, and with titan buff, nearly a white, phthalo green's mixing line rises from the parents' chromas of 9 and 15 to 47 at 45 percent titan buff. Leaving titan buff out, 6 of the 300 pairs of calibrated paints have a best mixture that beats both parents by at least one unit of chroma, 3 by three or more, and none by more than six. Okumura's test of the same kind of model on 27 two-paint mixtures found a mean error of 2.2 units of ΔE_{00} and a worst of 8 (Section 2.6). Chroma is not conserved by mixing, and it is not even monotonic along a mixing line. What equation (20) conserves is the band-by-band ordering of K/S , and chroma depends on the ratios between bands.

Glazes against tints (Section 3.6). The glaze series is computed by the Beer–Lambert law of equation (7) over the model's white, and the tint series by the Kubelka–Munk law with the same white, both from the same absorption spectrum per gram. A glaze of thickness u over a ground of internal reflectance R_g reflects $R_g e^{-2uK(\lambda)}$ inside the surface. The ratio of its reflectance in the passed band to that in the absorbed band is $e^{2u(K_{\text{abs}} - K_{\text{pass}})}$, which grows without bound as the glaze thickens, so the glaze's purity is limited only by the pigment's own absorption contrast and by how dark one is willing to go. A tint has, in the absorbed band, $K/S = (1 - \sigma)m_{\text{abs}}$ with σ the white's share of the scattering, by equation (21). A tint light enough to be useful has σ near one, which pulls the absorbed band onto the steep part of the Kubelka–Munk curve, where a K/S of 2 already reflects 17 percent inside the paint, so the tint's purity is limited by the white. At $L^* = 50$ and 65 the glaze and the tint have chromas of 87 and 55, then 67 and 46, for quinacridone magenta; 76 and 46, then 82 and 47, for phthalo green; 72 and 44, then 50 and 35, for dioxazine; and 50 and 25, then 42 and 22, for burnt sienna. The magenta glaze at $L^* = 50$ has a hue of 341° against the tint's 346° . In its absorbed band, 500 to 580 nm, the tint reflects 10 to 14 percent and the glaze 5 to 10; above 640 nm the glaze reflects 94 to 96 percent and the tint 78 to 95. The glaze numbers are an upper bound, for the reasons given in Section 3.6, but the gap of 20 to 30 units of chroma at equal lightness is far larger than those corrections.

What white does to a hue (Section 3.7). In Okumura's ladders, from the masstone to the palest tint at ten to twenty percent paint by weight, the organic reds move toward magenta

by 20 to 30 degrees, the blues toward cyan by 14 to 57, and the yellows and the earths toward yellow and yellow-green by 4 to 11; phthalo blue goes from 300° to 244° , phthalo green from 234° to 185° , dioxazine from a masstone so dark that its hue of 1° means nothing to a violet at 304° , green gold from 112° to 106° and red oxide from 37° to 25° [59]. The rule that white opens the bands in order of absorption is equation (22) read for hue: the tint's K/S at every wavelength is K_p/S_w times one number that falls as white is added. In a dark masstone a band with a large K/S reflects about $S/2K$, so a band that absorbs ten times more is ten times darker and the strongest bands are black whatever their differences. In a pale tint every band is near the top of the curve, where the reflectance is $1 - \sqrt{2K/S}$ to a good approximation, and the same two bands differ by a factor of $\sqrt{10}$, about three, in how far they fall short of the white. Ultramarine's masstone K/S is about 1.5 at 440 to 470 nm, 10 at 470 to 500 nm and 50 to 60 across the green, yellow and red, and its hue moves from 294° toward cyan. Green gold's K/S is about 20 below 470 nm and 2 to 3 above 600 nm; by half white its red is level with its green hump at 59 percent while the blue is at 10, and its hue has gone from 117° to 104° . Yellow ochre's K/S is about 1 in the green against 3 to 5 in the blue, and its hue goes from 70° in masstone to 75° in the tint in the model, and from 71° to 79° in the ladder. The white's reflectance [71] is flat at 95 percent from 450 nm to 700 nm and falls below 430 nm to 45 percent at 400 nm, the absorption edge of rutile, whose band gap of about 3.0 electron volts corresponds to 410 nm [43, 57]; scaled to Golden's lightness of 98.3 it gives $b^* = +1.9$, against 1.67 on Golden's chart [25]. Rutile particles of about $0.25\ \mu\text{m}$, by a Mie calculation with the measured refractive index of rutile [21, 4], scatter 128 percent of their 550 nm value at 400 nm and 67 percent at 700 nm, and the Lawrence Berkeley measurements of a titanium white paint give about 800 per millimeter at 400 nm against 400 at 700 nm [42, 43]. By equation (20) a colorant's absorption is divided by $S_w(\lambda)$ at each wavelength, so it counts half as much in the blue as in the red. In Figure 19(d) a gray of ten percent carbon black has $b^* = -2.9$ with the real white and $+1.3$ with a white that scatters every wavelength alike, a difference of $4.6\ \Delta E_{00}$; the two-percent gray differs by 4.1, a tint of burnt umber by 2.8, with $b^* = +10.5$ against $+14.6$, tints of pyrrole red and ultramarine by 2.2, and a tint of hansa yellow medium by 1.0. Okumura's gray of five percent carbon black in Matte Fluid white has a hue of 257° and a chroma of 2.5 [59]. A white on its own shows none of this, since it absorbs almost nothing for its scattering to work against. The comparison of Figure 19(d) takes the white's scattering from the calculation and the Berkeley measurements, because the tint ladders cannot tell a white that scatters blue more from a black that absorbs red more: every fitted scattering is relative to the white's, so a bluish gray in a ladder is reproduced whatever its cause. Other whites differ. Zinc white, whose band gap is near 370 nm, has no visible tinge and scatters far less, and anatase, the other form of titanium dioxide, is whiter but chalks and is little used [57, 43, 56]. The white's scattering shifts a tint by one to four units of b^* , which is three to six degrees of hue for a red or a blue.

The split-primary test (Section 3.8). Each pair of paints is mixed in 201 proportions by weight, from all of one paint to all of the other. Each mixture is brought to the target lightness with titanium white, and the one whose hue comes closest to the target is kept; its chroma is the best the pair can do at that hue and lightness. The targets are a middle green at $h_{ab} = 155^\circ$ and $L^* = 60$, an orange at 58° and $L^* = 65$, and a violet at 315° and $L^* = 45$. A paint's lean is the hue of its tint at $L^* = 60$, or of its masstone where that is lighter already, and the hues quoted below are of those tints, or of the masstone for a paint already lighter than that. With the palette's six paints the greens are 42 for hansa yellow medium with phthalo blue (green shade),

24 for hansa yellow medium with ultramarine, 21 for diarylide yellow with phthalo blue and 11 for diarylide yellow with ultramarine. The oranges are 77 for diarylide yellow with pyrrole red, 68 for diarylide yellow with quinacridone magenta, 64 for hansa yellow medium with pyrrole red and 52 for hansa yellow medium with quinacridone magenta. The violets are 40 for quinacridone magenta with ultramarine and 37 with phthalo blue, and 15 for pyrrole red with ultramarine and 13 with phthalo blue. So the yellow's lean is worth 13 to 21 units in the greens and the blue's 10 to 18; in the oranges the yellow's is worth 12 to 16 and the red's 8 to 12; in the violets the two reds differ by about 25 and the two blues by 2 or 3. A comparison takes two paints of one family, mixes each with the same partner for the same secondary, and asks whether the one whose lean is nearer the secondary makes the higher chroma; a difference of two units or less counts as a tie. The partners are hansa yellow medium for the reds' oranges and the blues' greens, pyrrole red for the yellows' oranges, ultramarine for the reds' violets, quinacridone magenta for the blues' violets and phthalo blue for the yellows' greens. Over all the calibrated paints, the 38 comparisons between the more vivid paints of each family split 26 for the paint that leans toward the secondary, 9 ties and 3 for the paint that leans away; the three are quinacridone magenta over quinacridone crimson for oranges, naphthol red medium over the crimson for violets, and ultramarine over cobalt blue, 24 to 21, for greens. The earths and Payne's gray go against the rule in 21 of the 42 comparisons they enter.

The mechanisms all come from equation (20): in each band the mixture's K/S is an average of the parents' masstone values m_i , each weighted by the parent's share of the mixture's scattering, so it lies between them (Fact 3.2), and in a band one parent absorbs it is that parent's m diluted by the other's share, equation (21). The chroma of a secondary is therefore set by the light both parents reflect in the secondary's band, by how dark the mixture is before the white that brings it to the target lightness, and by the weight each parent's m receives in each band. The numbers behind each case follow.

Reds for oranges, with hansa yellow medium, where the crimson's lean of 357° is toward orange beside the magenta's 342° and toward violet beside the naphthol's 2° : quinacridone magenta (342°) gives 52, quinacridone crimson (357°) 46, naphthol red medium (2°) 65, pyrrole red (14°) 64 and red oxide (27°) 35. The two quinacridones reflect 4 percent of the green band each. The crimson reflects 4 percent of the band from 400 to 440 nm against the magenta's 7, and 17 percent beyond 640 nm against 50. Before any white the crimson mixture is at $L^* = 45$ and needs 44 percent white to reach 65; the magenta mixture is at 49 and needs 35 percent. The red oxide mixture at the target is 44 percent red oxide by weight, and red oxide supplies half the scattering in the green band, 70 percent in the orange and nearly all in the red, so by equation (21) the mixture's orange and red are mostly red oxide's own, which in masstone reflects 21 and 33 percent there. The orange needs only 5 percent of naphthol red or 8 percent of pyrrole red, and the two absorb the green band about equally.

Yellows for oranges, with pyrrole red: yellow ochre (71°) gives 37, hansa yellow medium (83°) 64 and diarylide yellow 77. Ochre reflects 39 percent of the orange band and 40 of the red, against hansa yellow medium's 81 and 87. Its mixture with pyrrole red is at a lightness of about 52 and needs 28 percent white to reach 65; diarylide yellow's is at 66 and needs none. The hue of ochre's tint moves from 71° at $L^* = 60$ to 77° at 80 and 82° at 90.

Reds for violets: naphthol red medium (2°) gives 24 with ultramarine and 27 with cobalt blue, and quinacridone crimson (357°) 19 and 21. The crimson reflects 4 percent of the violet band, as

naphthol red does, 6 percent of the orange band against 17, and 17 percent of the red against 72; the two measured masstones have lightnesses of 26 and 38. Pyrrole red (14°) gives 15 with ultramarine. Quinacridone magenta, which reflects 7 percent of the violet band, gives 40.

Blues for greens, with hansa yellow medium: cerulean blue (257°) gives 25, ultramarine (282°) 24, anthraquinone blue 24, cobalt blue 21 and phthalo blue (250°) 42. Cerulean reflects 15 percent of the green band and ultramarine 4. Cerulean has a chroma of 37 in masstone and 33 in its tint, and the mixture at the target is 82 percent cerulean. The phthalo mixture is 27 percent phthalo, which supplies about 3 percent of the scattering in the green band, so its absorption there hardly enters, while its K/S in the red is large enough that this small weight still removes the yellow's red. Hansa yellow medium reflects 41 percent of the green band. The yellows give greens of 49 for green gold, 42 for hansa yellow medium, 21 for diarylide yellow, 19 for yellow ochre and 16 for raw sienna, in the order of their lean.

For violets with quinacridone magenta, cerulean blue (257°) gives 38, anthraquinone blue (269°) 38, phthalo blue 37, ultramarine 40 and cobalt blue 41. The best mixtures are 87 percent magenta with anthraquinone blue and 91 percent with phthalo blue. The six calibrated blues give violets from 29 for Payne's gray to 41 for cobalt blue.

The gallery (Section 3.9). The hue angles here are those of tints at $L^* = 60$ unless a masstone is named. The fourteen paints of Figures 21 and 22, in order of hue, are hansa yellow medium, diarylide yellow, burnt sienna, pyrrole red, naphthol red medium, quinacridone magenta, dioxazine purple, ultramarine blue, cobalt blue, cerulean blue, phthalo blue, phthalo green, chromium oxide and green gold. In the balanced grid each pair is mixed in the proportion at which the mixture is equally far in ΔE_{00} from both parents, and a dot marks a pair whose tinted mixing line passes within a chroma of 8 of gray.

Across the hansa yellow medium row of Figure 21, half-and-half by weight, the mixtures are: with diarylide yellow a chroma of 92; with burnt sienna 36 at 64° ; with pyrrole red 69 at 33° , a red-orange, since the red is the stronger paint; with naphthol red medium 55 and with quinacridone magenta 47, both at 33° ; with dioxazine 7, an olive gray; with ultramarine 24 at 133° ; with cobalt blue 29 at 123° ; with cerulean 33 at 128° ; with phthalo blue 14 at 156° ; with phthalo green 31 at 150° ; with chromium oxide 43 at 124° ; with green gold 60 at 98° . With two parts of white the same cells read 77, 39, 51, 51, 41, 7, 31, 36, 38, 37, 55, 41 and 71. The quinacridone magenta and dioxazine rows have chromas of 3 to 14 against most partners in masstone and no more than 21 against any. Tinted, magenta with ultramarine is a violet of chroma 39 at 306° , magenta with phthalo blue 35 at 282° and dioxazine with cobalt blue 46 at 303° .

The balancing proportions of Figure 22 include diarylide yellow with burnt sienna at 58 to 42, with pyrrole red at 91 to 9, with quinacridone magenta at 80 to 20, with phthalo blue at 85 to 15, with cobalt blue at 30 to 70 and with chromium oxide at 76 to 24; hansa yellow medium with phthalo blue at 94 to 6 and with cerulean at 51 to 49; quinacridone magenta with phthalo blue at 98 to 2 and with ultramarine at 92 to 8; dioxazine with ultramarine at 10 to 90. The pairs marked with a dot are burnt sienna with ultramarine, cobalt blue, cerulean, phthalo blue or phthalo green; diarylide yellow with cobalt blue or cerulean; hansa yellow medium with dioxazine; pyrrole red, naphthol red medium and quinacridone magenta with chromium oxide, and pyrrole red with phthalo green; dioxazine with chromium oxide or green gold.

Along the lines of Figure 23, hansa yellow medium to diarylide yellow runs from a chroma of 96 to 90 with no dip; diarylide yellow to pyrrole red drops from 90 to 72 at the first step and holds between 68 and 70 from there; phthalo blue to cerulean runs from 24 up to 38; cerulean to phthalo green from 37 down to 9. With white, pyrrole red to quinacridone magenta goes from 17° to 344° , and dioxazine to ultramarine from 306° to 284° . Along the lines of Figure 24, diarylide yellow to dioxazine falls from 90 to 8 by half way, and the tinted row stays below 15 from 40 to 70 percent; hansa yellow medium to ultramarine passes through greens of 51, 40, 34, 29, 24, 21, 17, 14 and 9, tinted 54 down to 17; naphthol red medium to phthalo blue is down to 2 by 30 percent; burnt sienna to ultramarine falls to 5 by 30 percent blue and to 2 by 60; yellow ochre to dioxazine stays at 6 or 7 from 20 to 80 percent.

For Figure 25 each of the twelve paints is brought to $L^* = 60$ with white, and every other chromatic calibrated paint, also at $L^* = 60$, is tried as a partner in every proportion; the partners marked are those that bring the chroma below 4. Ultramarine (282° , opposite 102°) is neutralized only by burnt sienna (40°), at about one part blue to two of sienna, leaving a chroma of 1.5. Cobalt blue (opposite 95°) is neutralized by partners at 40° and 72° , best by burnt sienna; phthalo blue (opposite 70°) and cerulean (opposite 77°) by burnt sienna alone. Diarylide yellow (72° , opposite 252°) is neutralized only by cobalt blue (275°), at about one part yellow to ten of blue. Hansa yellow medium is neutralized by nothing below a chroma of 4; dioxazine comes closest at 4.2. Burnt sienna (40° , opposite 220°) is neutralized by five blues from 250° to 282° , best by anthraquinone blue. Pyrrole red (opposite 194°) is neutralized only by permanent green light (159°), naphthol red medium by permanent green light and chromium oxide, quinacridone magenta (opposite 162°) by greens from 145° to 159° , and phthalo green (182° , opposite 2°) by red oxide (27°). For the blues the mixing complement lies 23° to 62° toward red from the visual opposite.

The visual opposite is the direction through the gray center of the opponent plane (Section 1.3). A mixing complement is a paint whose K/S spectrum, weighted into the paint's own by equation (20), leaves a flat mixture, so it must be high where the paint's is low and low where it is high, with weights that balance. A yellow's reflectance is high above about 500 nm, so its complement must absorb everything above 500 nm and reflect below it. A blue reflects from 400 to about 520 nm with a tail into the red, so its complement must absorb that band and reflect the rest, which burnt sienna does and a yellow, reflecting the green part of the band, does not.

Darkening (Section 3.10). Each paint is darkened to a fixed lightness with carbon black, with a mixing complement and with burnt umber. Hansa yellow medium, to $L^* = 60$: 0.4 percent carbon black gives a chroma of 61 at 96° , 1.0 percent dioxazine 61 at 91° , 5 percent burnt umber 61 at 86° . Diarylide yellow, to 50: 2.7 percent black gives 38 at 82° , 39 percent cobalt blue 37 at 86° , 30 percent umber 41 at 69° . Pyrrole red, to 35: 2.5 percent black gives 44, 18 percent permanent green light 43, 40 percent umber 44, all at 27° . Permanent green light, to 30: 9 percent black gives 10, 22 percent quinacridone crimson 11, 56 percent umber 9. The chroma differences are within the model's error, except that umber keeps a few more units in the yellows: yellow ochre taken to 40, which is not in the figure, keeps 18 with umber against 13 with black or ultramarine. Adding white back to the three darkened reds, to $L^* = 55$, gives 32, 30 and 33.

A chromatic paint's lightness comes almost entirely from its passed band, since the absorbed bands return little light, so any darkener that brings it to a given lightness has brought the passed band to about the same reflectance. The chroma, the contrast between the passed band

and the rest, then comes out about the same, because the rest was dark already and can only get darker. By equation (20) black raises the mixture's K/S in every band in proportion to its weight there; a complement raises it in the passed band and leaves the already dark bands nearly alone; umber raises it most at the short wavelengths. Once the passed band is fixed, these differences decide the hue. Carbon black as fitted absorbs more at the red end than at the blue, because the fit put the bluish cast of its tints into the black's absorption as much as into the white's scattering (Section 3.7), so it takes more red than blue from a yellow and turns it toward green. UMBER absorbs the blue and holds the yellow nearest its own hue. Dioxazine absorbs in the yellow's passed band itself and moves hansa yellow medium's hue less than black does.

Matching by computer (Section 3.11). The four ColorChecker patches of Figure 27 are matched by least squares on their CIELAB coordinates under D65, with three Golden paints from a list of fifteen and titanium white. Within $1 \Delta E_{00}$ under D65, 117 recipes match dark skin, 96 match foliage, 111 match blue sky and 46 match orange. The figure compares, for each patch, the recipe whose reflectance curve lies closest to the target's with the one whose curve lies farthest, by their ΔE_{00} under illuminant A and under F11. Dark skin: 87 percent burnt sienna with a little hansa yellow medium, white and carbon black, 0.1 and 0.5, against cobalt blue with hansa yellow medium and pyrrole red, 3.5 and 2.0. Foliage: yellow ochre with hansa yellow medium and ultramarine, 0.3 and 2.2, against cobalt blue with hansa yellow medium, 3.7 and 6.6. Blue sky: ultramarine with white and a trace of black, 1.2 and 1.5, against cobalt blue with a little pyrrole red and green gold, 4.5 and 6.1. Orange: diarylide yellow with a little red oxide and pyrrole red, 0.2 and 3.0, against hansa yellow medium with quinacridone magenta, 3.4 and 1.4. The difference under the second illuminant, for a pair that matches under the first, is the index of metamerism of Section 1.4 [11].

The industrial procedure is described by Klein and by Berns [39, 3]. A colorant's K and S cannot both be read from one opaque drawdown, since the masstone gives only their ratio (Section 2.1), so the calibration set for each colorant is a masstone, one or more tints in the white and, for translucent films, drawdowns over black and over white at known thickness. The white's S is fixed as the unit, each colorant's S follows from how fast its tints dilute, and its K from the ratio. This is what Section 2.6 did with Okumura's ladders, and what Okumura and Berns did at full spectral resolution in building their database of artists' paints for this purpose [59, 51]. Matching is then an inverse problem: find concentrations c_i such that the mixture's tristimulus values equal the target's, three equations in as many unknowns as there are colorants, solved by iteration from a starting guess because the reflectance is a nonlinear function of the c_i through equations (20) and (8). With three colorants and a white there is usually a one-parameter family of solutions, which is why a hundred recipes match a single patch. The software ranks them by the index of metamerism, by cost and by how robust the recipe is to weighing errors; the trial batch is measured, and the recipe is corrected once or twice from the measured error. Matches within a unit of color difference are routine in industry after one or two corrections [39, 3]. The limit is the law's own accuracy, which Section 2.6 put at about two units for mixtures of colored paints.

4 What traditional color theory gets wrong

The color theory taught in art schools and painting manuals is a set of rules built around a wheel of twelve hues, with red, yellow and blue at its corners. Most of the rules are older than the

discovery of the three cones, and they carry the authority of long use. This part takes them one at a time and checks each against the measurements and mixtures of Parts 1 to 3. A few are simply wrong. Others hold, but for a different reason than the one taught, or only in a narrower sense. The aim throughout is to say which questions the rules really answer and which they only seem to.

4.1. What makes a paint a primary. Painters learn that red, yellow and blue are the primary colors: three colors that cannot be mixed from any others, and from which all the others can be mixed. The word primary is used for three quite different things, though, and the wheel runs them together. The eye has three kinds of cone, but the cones do not see three colors. Each responds to a broad range of wavelengths, and the one usually called the red cone is most sensitive to a yellow-green light. Perception has four hues that look like nothing but themselves, red, yellow, green and blue (Section 1.3), yet they are elementary only to the eye: a yellow paint cannot be mixed from a red and a green. At the palette, the first half of the painter's definition is the useful one. A primary is a paint that nothing else on the palette can mix. The second half fails, since no three paints mix everything, and Section 4.3 measures how far short they fall. Nothing in the eye or in the paint singles out red, yellow and blue.

Each meaning has its own history. The cones are the primaries of physiology. Their sensitivities overlap so broadly that no wavelength excites only one kind, and their peaks lie in the blue-violet, the green and the yellow-green [70]. Young and Helmholtz called their three receptor processes red, green and violet, and the names stuck. They name the lights that excite each kind of cone most selectively, and say nothing about what the cones see [78].

The elementary hues are the primaries of perception. They are Hering's four, which sit at the two ends of the eye's two color channels, red against green and yellow against blue. Each has a partner it can never be seen together with, so there is no reddish green and no bluish yellow. Three of the four can be seen in light of a single wavelength, while a red that is neither yellowish nor bluish needs a little short-wave light added to the long end of the spectrum [32, 35]. Yellow counts as elementary in this sense even though the eye makes it from the sum of two cone signals. The Natural Color System is built on these four hues together with white and black, and has no notion of mixing at all [29].

The mixing primaries are a third thing again, and they depend on what is being mixed. For lights they are any three whose mixtures cover the most of the chromaticity diagram, the map of colors with their lightness taken out (Section 1.7), which for screens means a red, a green and a blue near the two ends and the middle of the spectrum [36]. Printing inks use a cyan, a magenta and a yellow, each of which absorbs one third of the spectrum and passes the other two. For paints, in this loose sense, a set of primaries is whichever three paints reach the most colors. Red, yellow and blue became the painters' three in the eighteenth century, from Le Blon's three-color printing and from the look of the pigments then available, before anyone had separated the three meanings [41, 6].

On the palette, a primary is simply a paint that nothing else there can mix. A paint can be mixed from a set of others only if its color lies inside the region their mixtures reach, and that region is limited. At every wavelength a mixture's absorption divided by its scattering, the K/S of Part 2, lies between its ingredients' values (Fact 3.2), so no spectrum outside their range can be mixed, even though a tint can be more vivid than the paint it came from. Section 4.3 searches fifteen colorful calibrated paints for the three that reach the most colors at a middle lightness,

and finds hansa yellow medium, quinacridone magenta and phthalo blue. Figure 28 then checks the fifteen other calibrated single-pigment paints with some color against those three. That is a slightly different fifteen: it takes in the earths and chromium oxide, which the search left out, and leaves out green gold and permanent green light, which are mixtures of pigments. Seven lie outside the three's reach: diarylide yellow, pyrrole red, naphthol red medium, dioxazine purple, ultramarine, cobalt blue and phthalo green. The furthest out is diarylide yellow, about twice as vivid as anything the three can mix at its hue and lightness. Of the eight that fall inside, four are earths, which are dull to begin with. Cerulean blue is inside because phthalo blue makes a better cerulean than cerulean is. Anthraquinone blue counts as inside only because the three come very close to it. The last two are quinacridone crimson and chromium oxide. Each of the seven is a primary in the sense that matters at the palette, and the appendix to this part (Section 4.11) gives the test and the numbers for every paint.

fifteen single-pigment paints against the best three: hansa yellow medium, quinacridone magenta, phthalo blue

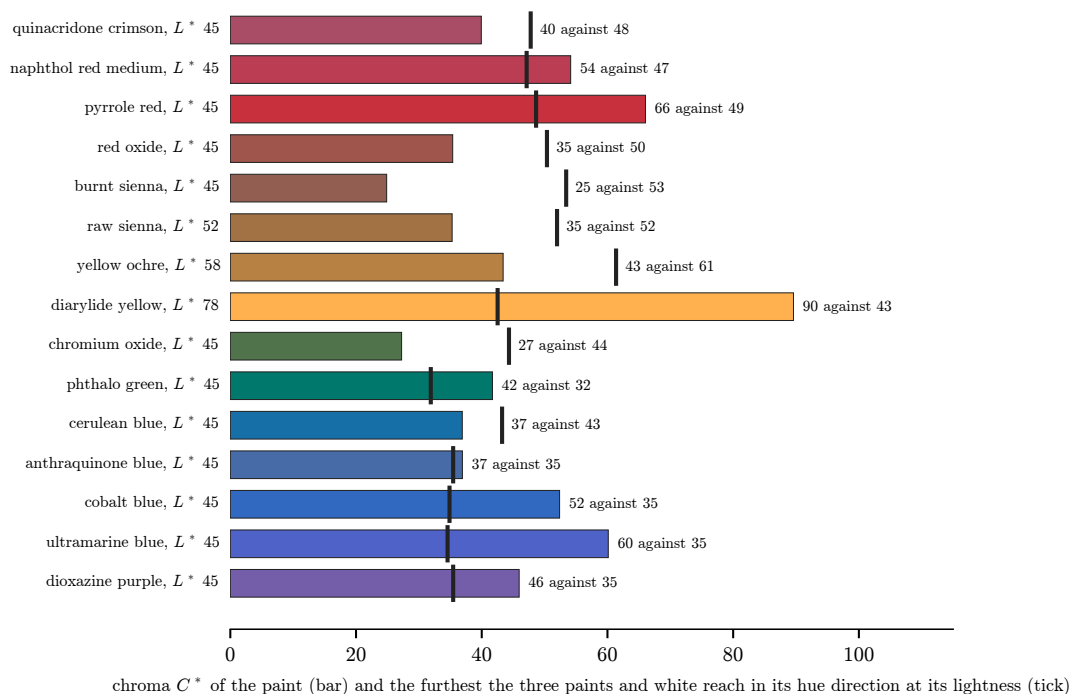


Figure 28: Paints that the best three cannot mix. Each bar is the chroma of one of the fifteen other calibrated single-pigment Golden paints with some color, taken at its own lightness, or tinted with white to a lightness of 45 if it is darker than that. The tick on each bar marks the furthest that hansa yellow medium, quinacridone magenta, phthalo blue and white reach in the same hue direction at the same lightness. A bar that passes its tick is a color the three cannot mix.

The number three came from the cones, and from the way lights mix. Grassmann showed in 1853 that lights mix by simple addition [26]. With the eye's three kinds of cone, that means three well-chosen lights can match most colors, though no three can match them all. The number three was carried over to paint by analogy.

4.2. Vivid colors come from broad bands. A pure yellow or a pure blue, in the way painters use the words, would be a paint that reflects a single hue, and the best pigments are supposed to come closest. No paint does, and the best pigments are the ones that stray furthest. A vivid yellow reflects the whole long half of the spectrum. Of the light cadmium yellow medium returns, as the eye weighs it, about a third comes from wavelengths that look green on their own, a third from the yellow ones and a third from the orange and red. A surface that reflected only the yellow part of the spectrum would be no brilliant yellow. It would be a dark mustard, only about as light as a mid gray, and a surface that reflected only a sliver around the yellowest wavelength would be darker still, a brown. Yellow is light because it is broad, and the same holds, less dramatically, for every hue: to be bright a surface must reflect a wide band of wavelengths, and a wide band always takes in the neighboring hues.

The first step of Figure 29 cuts the spectrum into four bands and measures how much of the light cadmium yellow medium returns, as the eye weighs it, comes from each. The violet and blue supply almost nothing and the other three bands about a third each, so two thirds of what makes this yellow bright is light that would be called green or orange if it arrived alone. The second step computes the colors of imaginary surfaces that reflect one band completely and nothing else (the numbers for every band are in Section 4.11). The yellow band of the spectrum gives the dark mustard, vivid but dark, since a yellow only as light as a mid gray no longer looks like a clear yellow. A surface that reflects every wavelength longer than 500 nm, from the green to the red end, is light and very vivid, and that is roughly what a cadmium yellow is.

The third step, in panel (c), starts from that sliver in the yellow, the brown, and widens it on both sides. As it widens the surface grows lighter, and it becomes as light as cadmium yellow medium only once the band is about a hundred nanometers wide, reaching from the green into the red. The chroma is highest at about that width too, and falls as the band goes on to swallow the whole spectrum.

How light a surface looks depends on how much light it returns, weighted by the eye's sensitivity. That sensitivity is a broad hump centered in the yellow-green, so a surface can be light only by reflecting a good part of the hump, which means reflecting from the green through the orange. Chroma comes instead from the differences between the cone signals, and a narrow band gives large differences, so the yellow band of panel (b) is vivid for all its darkness. The colors that are both light and very vivid are the optimal colors of Section 1.8, the most vivid any surface can be at each lightness, and MacAdam showed that at high lightness they are broad bands of the spectrum [47].

The last step, panel (d), looks at the same thing from the side of the cones. The narrow yellow band and the broad yellow both excite the long-wave and middle-wave cones and leave the short-wave cones alone; the broad one simply excites them more. Yellow is the hue the eye gives to any light that drives those two kinds of cone together and leaves the third alone, whether that light is a narrow band near 580 nm or the whole long half of the spectrum. The idea of a pure hue comes from the spectrum itself, where each wavelength has one hue and a narrow band of light can be intensely colored. It does not survive the move to surfaces, which must be broad to be bright, or to pigments. A pigment absorbs light by raising the energy of its electrons, and in a solid the vibrations of the molecules smear each of these absorptions into a broad band [57]. A painter who looks for a pure yellow is looking for a dark one.

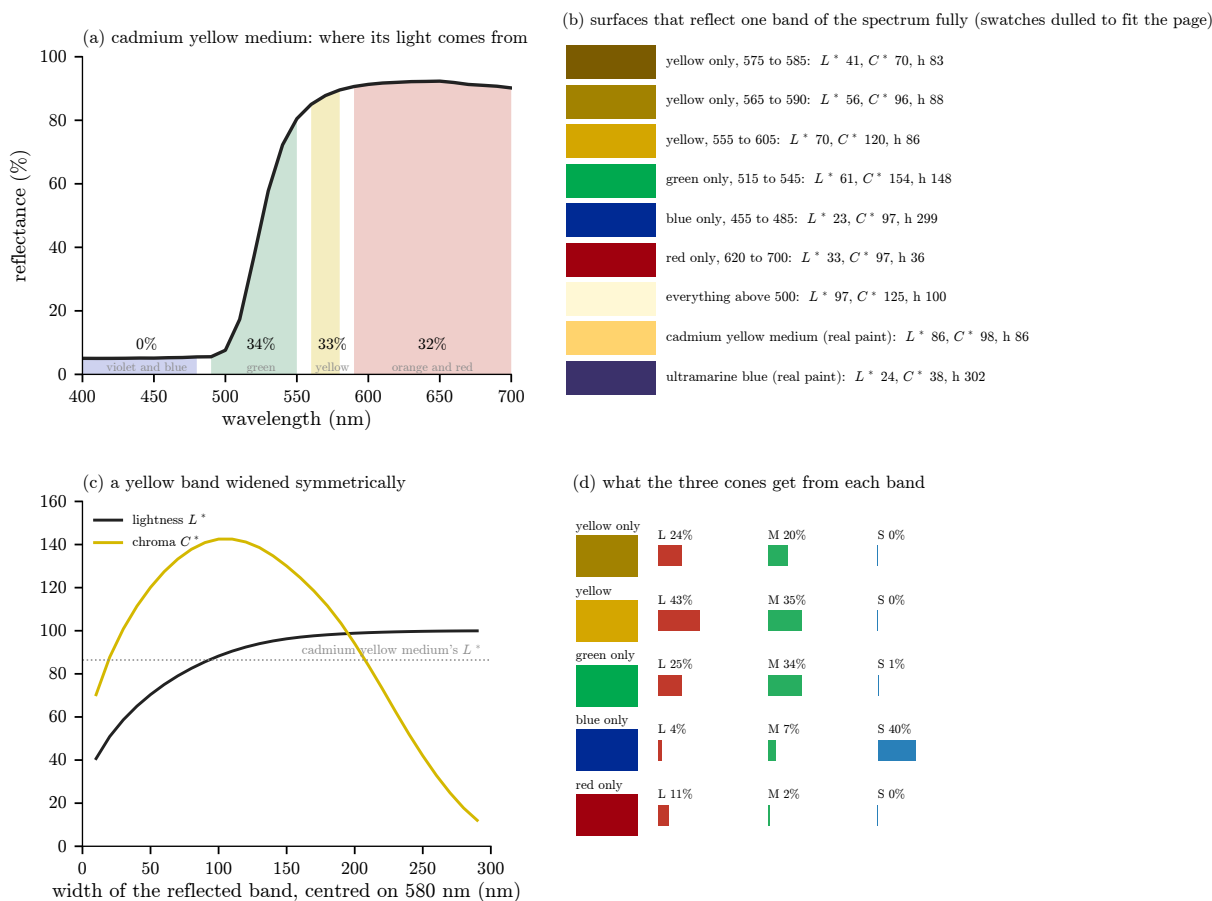


Figure 29: No pure hue. (a) Cadmium yellow medium's reflectance, with the spectrum divided into four bands and the share of the light the paint returns, as the eye weighs it, that each band supplies. (b) Imaginary surfaces that reflect one band of the spectrum fully and nothing else, with their lightness, chroma and hue; the swatches are printed with their chroma reduced to what the page can show. (c) A band centered on 580 nm widened on both sides: its lightness and chroma. (d) What the three kinds of cone receive from each band, as a fraction of what they receive from white.

4.3. Three colors cannot mix all colors. No three paints, with or without white, can mix every color, and they fall far short. Imagine every color a surface could possibly have at one lightness, laid out on the color plane of Section 1.7, with gray at the center and the most vivid colors furthest out. At a middle lightness the best three paints reach about a sixth of that area, and all 26 calibrated paints together reach not quite a quarter. The missing colors are not exotic. They are the scarlet reds, the deep yellows, the vivid greens and the deep blues and violets of single pigments. Lights do better, for reasons given at the end of this subsection, though even they cannot mix every color.

Figure 30 draws the region that three paints and white can reach at three lightnesses, for two choices of the three. The red-yellow-blue set is hansa yellow medium, pyrrole red and ultramarine. The other set is hansa yellow medium, quinacridone magenta and phthalo blue (green shade), a yellow, a magenta and a green-blue, close to the printer's cyan, magenta and yellow. A search

through every set of three from fifteen colorful calibrated paints, looking for the one that reaches the most at a middle lightness, picked this second set itself. Around both lie the region that all 26 calibrated paints reach and the limit of all possible surface colors.

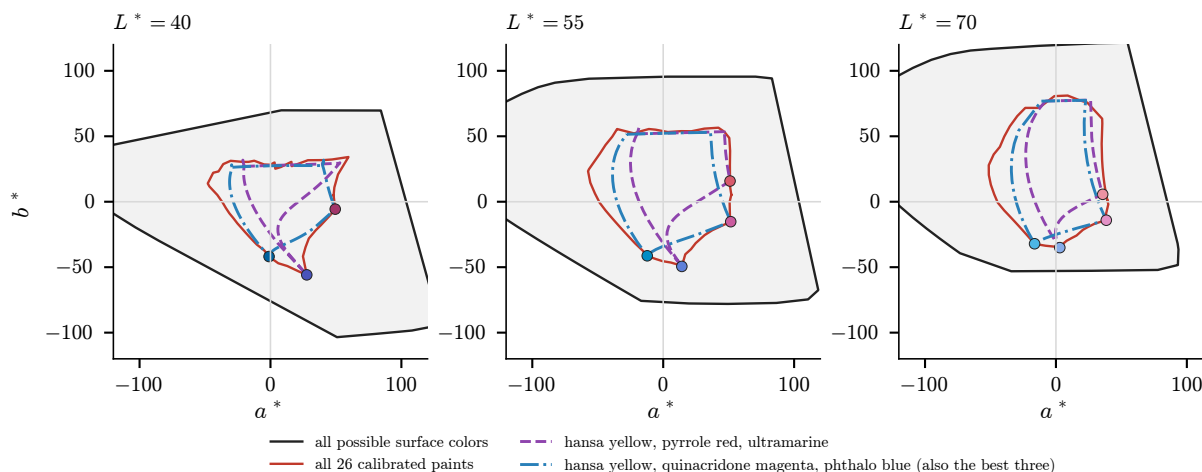


Figure 30: Three paints and white at three lightnesses, seen on the color plane with gray at the center. The outer line is the limit of all possible surface colors [47], the red line the region reached by mixtures of the 26 calibrated paints with white, and the two inner regions what two sets of three paints and white reach: a red-yellow-blue set, and a cyan-magenta-yellow set, which a search at a middle lightness also found to be the best three. The dots are the three paints of each set, brought to the lightness with white where they are darker than it.

The shapes show what is missing. The red-yellow-blue region has no violet corner, because its red and blue mix to gray, and its greens are dull. The cyan-magenta-yellow region has violets and greens, but it loses the oranges and the scarlet reds, which its magenta cannot reach. Both regions have sides that curve inward, because most mixing lines between two paints sag toward gray, and neither fills the region of the 26 paints, which is itself under a quarter of what surfaces can do.

The limit comes from Part 3. At every wavelength a mixture's K/S lies between the smallest and the largest of its ingredients' (Fact 3.2), so a set of paints can never reach a spectrum outside that range. And the way K/S turns into color bends most mixing lines between colored paints toward gray (Principle 3.1), so where they bend, the region the paints reach is smaller than the straight-sided shape joining their colors. A few lines bow outward instead: those from a yellow to a blue, and those from white to a dark transparent paint, whose tints are more vivid than the paint itself (Section 3.4). How the regions are drawn, and their areas at each lightness, are in Section 4.11.

Mixing two lights just adds them, so the mixtures of three lights fill the straight-sided triangle between them on the chromaticity diagram. Even so, no triangle holds every color, because the edge of the diagram, where the single wavelengths lie, curves outward. An ordinary monitor's three lights enclose about a third of the diagram [78, 36]. Pointer measured the colors of some four thousand real surfaces, and the region he found is still the standard against which displays are judged [61]. Paint is worse off than a display, since its primaries are themselves surfaces and its mixtures bend toward gray.

4.4. Cyan, magenta and yellow do better than red, yellow and blue. If a painter must choose three paints, something close to the printer's three serves better than the painter's: a yellow, a magenta-red and a green-blue in place of a yellow, a red and a blue. The reason is easiest to see with the visible spectrum cut into thirds, named after the light in them: blue, green and red. A yellow pigment absorbs the blue third and passes the other two. A magenta absorbs the green third, and a cyan the red third. Any two of these pass one third in common, and their mixture keeps what both pass. Yellow and magenta share the red third and make a red-orange; yellow and cyan share the green and make green; magenta and cyan share the blue and make a blue-violet. Printing inks are chosen for this reason [3].

A red pigment absorbs two thirds of the spectrum, the blue and the green, and passes only the red. A violet-blue absorbs the green and the red, with a little of the red leaking through, and passes the blue. A red and a violet-blue share nothing but that leak, and they mix to the gray of Figure 13. Red and yellow share the red third and mix well. Yellow and blue share a little green, where the edge of the yellow's reflectance overlaps the tail of the blue's, and they mix to dull greens. Of the three secondary colors, the mixtures of two primaries, the red-yellow-blue set makes one well, one dully and one not at all, while the cyan-magenta-yellow set makes all three.

With the calibrated paints the advantage is real, though smaller than the picture suggests. Hansa yellow medium, quinacridone magenta and phthalo blue cover about half as much again of the color plane as hansa yellow medium, pyrrole red and ultramarine, averaged over lightnesses from fairly dark to fairly light, and about twice as much in the dark colors (Figure 30 shows three of those lightnesses). The red-yellow-blue set wins in two narrow wedges, the scarlets and the violet-blue, which are its own red and blue. The magenta set wins across whole regions of the circle, the violets and the greens; at a violet near dioxazine purple's hue and a fairly dark lightness, for one, it mixes colors with more than twice the chroma.

The real pigments are not the ideal blocks of the picture. Quinacridone magenta reflects some violet and is dark, phthalo blue only approaches a cyan and is dark too, and the printer's inks are made transparent and thin, which paints are not. That is why the magenta set's advantage is smaller than the blocks would suggest, and it loses the scarlets, which need a fourth paint of their own. The painters' six-paint palette, which adds a scarlet and a violet-blue to the three, is a recognition of this, and Section 3.8 tested its rule.

4.5. Color bias fails as a concept. The split-primary palette explains itself with the idea of color bias. Every paint is said to lean toward one of its neighbors on the wheel, a blue toward green or toward violet, a red toward orange or toward violet, a yellow toward green or toward orange, and the lean is supposed to decide its mixtures: a blue that leans toward green should make clean greens and dull violets. Section 3.8 tested the palette's six paints and some of their relatives two at a time, and found the rule right for the six and wrong for several of the others. Here the idea itself is put to the test, on every calibrated blue, red and yellow at once.

For each paint the lean is the hue of its tint, the paint with enough white to bring it to a middle lightness, since a dark masstone hides its hue (Section 4.9). Each paint is then mixed in every proportion with a fixed partner, a yellow for the greens for example, and the chroma of the mixture that lands on a chosen green, orange or violet is recorded; the partners and the target colors are listed in Section 4.11. Figure 31 plots the lean against the chroma. If the lean decided the mixtures, the points for each family would climb or fall in a line.

Only the yellows come close. Apart from the two earth yellows, their greens with phthalo blue

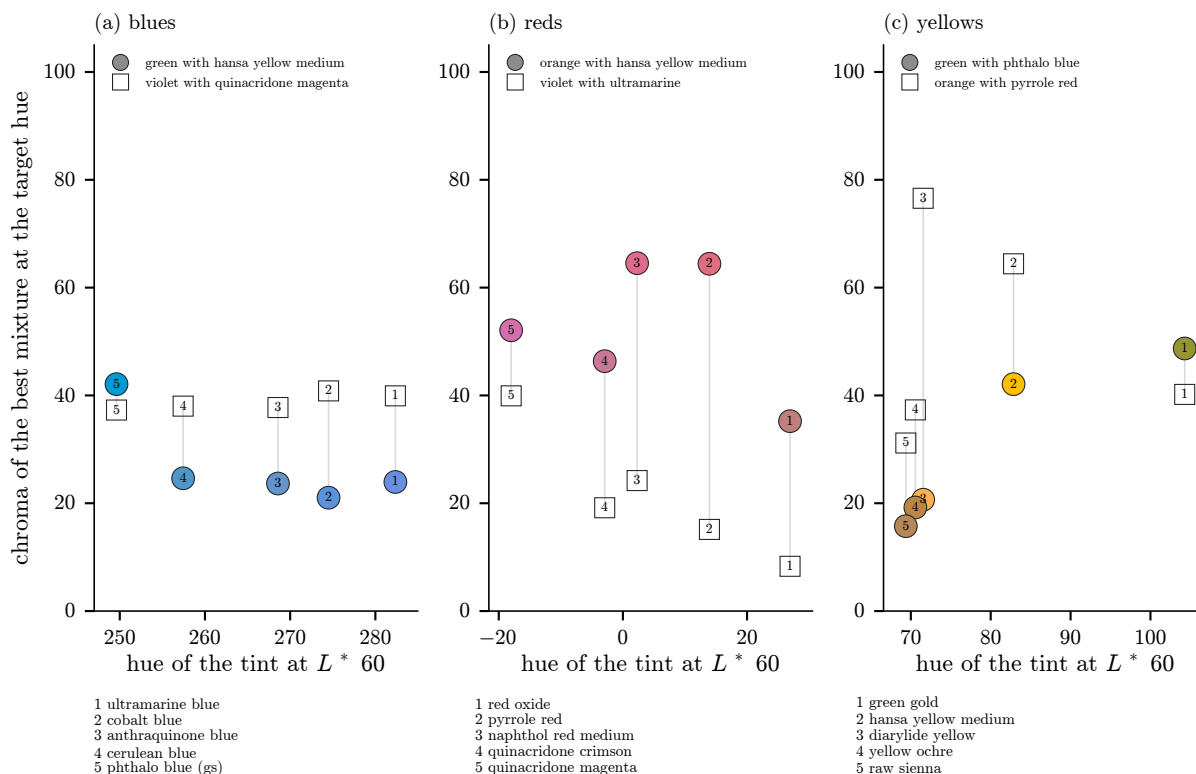


Figure 31: The lean of a paint against its mixtures, for the calibrated blues (a), reds (b) and yellows (c). Payne’s gray, which is nearly black, and burnt sienna, an orange between the reds and the yellows, are left out. Across: the hue of each paint’s tint at a lightness of 60 (or of its masstone, for the yellows lighter than that), which is its lean. Up: the chroma of the best mixture it makes with a fixed partner at a fixed hue and lightness, with filled circles for one secondary and open squares for the other. The numbers identify the paints in the keys below.

fall and their oranges with pyrrole red rise as the lean moves from green toward orange, and Section 3.8 showed why: a yellow’s reflectance is a single edge, and where the edge falls sets both its hue and its greens. The blues follow the lean only roughly, with large differences between blues of nearly the same hue and almost none in their violets. The reds hardly follow it at all, although with five reds that test is thin. Each failure comes from something the lean leaves out, as the tests of Part 3 showed.

A lean is one number, the hue, and a mixture depends on a whole curve. A mixture of two paints of different hues, such as a green from a yellow and a blue, is vivid in proportion to what both reflect in the band of wavelengths that gives the mixture its hue. A blue’s hue is set largely by the balance between its blue reflectance and the tail it has into the red, which pulls it toward violet. Its greens are set by how much green light it reflects, which is a separate matter. Cobalt blue leans toward violet because of that red tail, and the tail has nothing to do with how much green it reflects, which is what decides its greens.

A rule that works for yellows, roughly for blues and not for reds is a correlation, one that holds when a pigment’s reflectance happens to be a single edge. The better guide is to read the curve, or, lacking the curve, read the paint’s lightness and chroma as well as its hue, and expect the

middle of the spectrum to dominate any mixture across the circle [15].

4.6. Munsell’s circle against the equal-spaced wheel. The artists’ wheel sets out twelve hues at equal steps of thirty degrees, with red, yellow and blue at the corners of a triangle and the greens, blues and violets filling the space between. The wheel calls these equal steps. Measured with the hue angle of CIELAB, which was designed to follow the eye, they are far from equal. The third of the wheel from red to yellow covers less than a fifth of the measured circle, and the third from yellow round to blue covers more than half. The wheel stretches the oranges and crushes the greens and blue-greens, and it puts blue and blue-violet a full step apart where their paints are close neighbors.

To check this with real paints, Figure 32(a) puts the calibrated paint nearest each of the wheel’s twelve names on an outer ring, at the wheel’s equal steps, and on an inner ring at the CIELAB hue of its tint. There is no calibrated orange, so two earths, red oxide and burnt sienna, stand in for red-orange and orange. Neighbors on the inner ring are anywhere from a few degrees to a quarter of the circle apart. The wheel holds red, yellow and blue a third of the circle from each other, while their paints sit much closer from red to yellow and much farther apart from yellow round to blue. Any other reasonable choice of paints gives the same picture, because the unevenness is in the wheel itself.

The twelve-hue wheel descends from the color circles of the eighteenth century, which arranged the painters’ three primaries and their mixtures symmetrically because symmetry was the point [41, 6]. Itten’s version, the one most art students learn, says plainly that it is built from three primaries by mixing, with the secondaries and tertiaries placed between them by construction [37]. Munsell set out in 1905 to make a notation in which equal steps would look equal, in hue, in value (his word for lightness) and in chroma. His circle has no primaries. He chose five principal hues with five intermediates between them, so that the circle could be divided by tens and so that hues opposite each other would mix to gray on a spinning disk, and divided it into forty steps in all [54, 55]. In 1943 a committee of the Optical Society measured the Munsell samples, smoothed their spacing against the measurements and the judgments of many observers, and published a corrected set of colors, the renotation, which the system has used since [58]. CIELAB was later designed with the Munsell spacing as one of its targets [62, 41], so the two should agree fairly well, and Figure 32(b) shows that they do.

Panel (b) does the same for Munsell’s circle, placing each of its forty hues at the CIELAB hue of its Munsell sample, computed from the renotation. Its steps are not perfectly equal either. Some of the unevenness comes from CIELAB, whose hue angle follows judged differences of hue better in some regions than in others, the blues being the worst; this is one of the things the CIE’s formula for color difference of 2000 corrects [45, 23]. Still, Munsell’s largest step is less than twice its smallest, where the wheel’s largest is more than ten times its smallest (Section 4.11 lists them). The greens and blue-greens, which the wheel crowds into a quarter of its circle, get the third of Munsell’s that the eye gives them.

The inner ring of panel (b) shows where the calibrated paints fall: thick in the yellows and the reds, thick again in the blues, and thin in the yellow-greens and from blue-green round to blue, where there are few vivid single pigments. The wheel’s crowding of the greens may owe something to this, since a circle made from the paints at hand would have few greens to space out.

Munsell’s circle says how far apart two hues look, and says it well. A painter who wants to space hues evenly in a picture, or to judge how far a mixture has moved, should use it. The wheel is

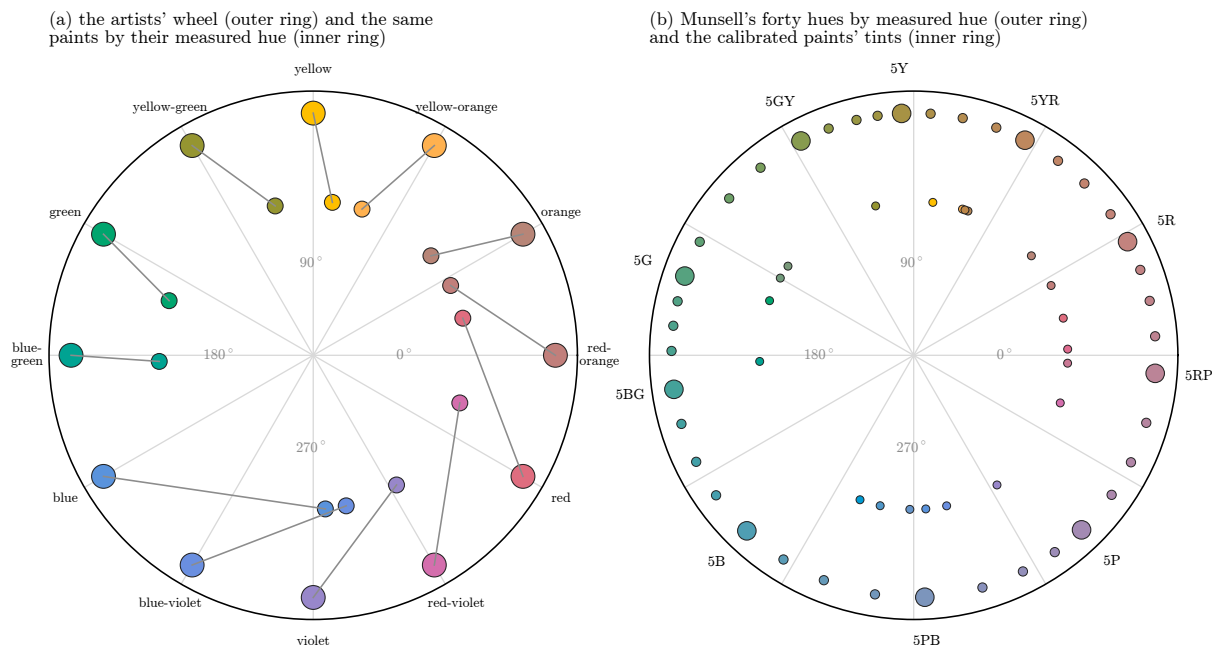


Figure 32: Two hue circles against measured hue. (a) The twelve names of the artists' wheel at the wheel's equal steps (outer ring), with the calibrated paint nearest each name, and the same paints at the CIELAB hue angle of their tints (inner ring). (b) The forty hue steps of the Munsell system at their CIELAB hue angles, computed from the 1943 renotation [58] at a Munsell value (lightness) of 6 and chroma of 6 under illuminant C, an older standard daylight, with the five principal and five intermediate hues named (outer ring), and the tints of the 21 calibrated paints with some chroma (inner ring); carbon black, Payne's gray, titan buff and the two umbers are left out.

meant to say which paints mix to which, and it does that only in part: its three primaries are not the best three (Section 4.4), and its leans do not decide mixtures (Section 4.5), although its pairs across the center turn out to be fair mixing complements with these paints (Section 4.7).

4.7. Visual complements are not mixing complements. The wheel's pairs across the center, red and green, yellow and violet, blue and orange, are taught as complements in every sense at once: each pair is supposed to give the strongest contrast side by side, to be each other's afterimage (Section 1.5), and to mix to gray. With the calibrated paints the wheel's pairs turn out to be fair mixing complements. The hue the eye sees as opposite, though, is usually a different paint, and the contrast and the afterimage go with that one. A single wheel cannot give both, because the eye sets one kind of complement and the spectrum of the paint sets the other.

The visual complement comes from the eye's two color channels (Section 1.3). Two colors are opposite when they push both channels in opposite directions, which puts them on a line through gray on the color plane, half the circle of hues apart, to the accuracy with which CIELAB's angles follow the eye. For pyrrole red that is a blue-green, where the wheel says green, because pyrrole red sits a little off the red end of the red-green axis, toward yellow. For hansa yellow medium, which sits close to the yellow end of the other axis, it is a blue, where the wheel says violet, and for cobalt blue it is a yellow, where the wheel says orange. Hering's own pairs, red with green and yellow with blue, are the axes themselves, and they hold for the unique hues, not

for every pigment that carries their names.

A mixing complement depends on two reflectance curves instead (Section 3.9). The partner must absorb where the paint reflects and reflect where it absorbs, band by band, with matched strength, and the spectrum knows nothing of the eye's channels. For the blues the partner is an orange-brown, for the yellows a violet or a violet-blue, and for the greens a red-orange or a magenta-red. The wheel's yellow and violet, and its blue and orange, come close to this, since a yellow's neutralizer must reflect the violet-blue end of the spectrum alone and a blue's the orange-red end alone. Its red and green come close too with these paints, since permanent green light absorbs the long half of the spectrum that pyrrole red reflects, but a green's best neutralizer must absorb the middle of the spectrum, which a red does and a magenta does better. The two kinds of complement agree only where the eye's axes and the halves of the spectrum happen to line up, as they do for magenta and green and for violet and yellow-green. Elsewhere they differ by as much as 55 degrees.

Figure 33 sets the three kinds side by side for six paints that stand for the wheel's primaries and secondaries, with burnt sienna in place of the missing orange. Take hansa yellow medium. The wheel offers violet; the hue exactly opposite is a blue, nearest to cerulean; and the paint that brings it nearest to gray is dioxazine purple, a violet after all. Pyrrole red's visual complement is a blue-green near phthalo green, while its mixing complement is permanent green light, the wheel's own green, and cobalt blue's visual opposite is a yellow, while its mixing complement is burnt sienna, the wheel's orange. Only for dioxazine purple and permanent green light are the visual and the mixing complement the same paint, green gold for the first and quinacridone magenta for the second. The hues and proportions behind the figure are in Section 4.11.

The wheel's pairs were assembled from pigment practice as much as from theory. Chevreul's law of simultaneous contrast, which says how a color looks changed by the colors around it, gave the wheel much of its authority, and it is about the visual relation [10]. The painters who used the wheel to kill a color with its opposite were using the mixing one. Albers, who had no use for the wheel, taught complements by trial, with pairs of actual colored papers [1].

4.8. Three meanings of warm and cool. Yellows, oranges and reds are called warm, and greens, blues and violets cool, and every hue is said to come in warmer and cooler versions: a warm red leans toward orange, a cool one toward violet. The words carry real associations and are useful for talking about a picture. As a physical description of a color they have no fixed meaning, since three different versions are in use and they disagree. As a rule for mixing they are the bias rule of Section 4.5 under another name, with the same failures. A paint's warmth is not even fixed. In Figure 34(b) the reds move toward violet by about thirty degrees of hue as white is added, and the blues toward green by about forty, phthalo blue by about sixty.

Figure 34(a) draws the three versions on the measured hue circle. The painters' usual split puts the boundary between yellow-green and red-violet, with yellow, orange and red on the warm side and green, blue and violet on the cool. Itten, whose teaching fixed the modern usage, named red-orange the warmest hue and blue-green the coolest [37], which turns the boundary to run through the yellow-greens and the violets. The physicist's version is color temperature, the color of a glowing body as it gets hotter: from the orange-yellow of a candle flame through the white of daylight to the blue of a clear sky. Placed on the hue circle with daylight as the white, that line runs from yellow-orange to violet-blue [78], some way off Itten's axis at both ends. The three versions agree only that orange is warm and blue is cool. Under the usual split a lemon

the paint	its complement on the wheel	its visual complement	its mixing complement, and the gray
yellow: hansa yellow medium, h 83	on the wheel: dioxazine purple, h 303	opposite hue 263: cerulean blue, h 257	mixes to gray: dioxazine purple, h 303 $C^* 4$ 59:41
orange: burnt sienna, h 40	on the wheel: cobalt blue, h 275	opposite hue 220: phthalo blue, h 250	mixes to gray: anthraquinone blue, h 269 $C^* 0$ 85:15
red: pyrrole red, h 14	on the wheel: permanent green light, h 159	opposite hue 194: phthalo green, h 182	mixes to gray: permanent green light, h 159 $C^* 4$ 36:64
violet: dioxazine purple, h 303	on the wheel: hansa yellow medium, h 83	opposite hue 123: green gold, h 104	mixes to gray: green gold, h 104 $C^* 1$ 64:36
blue: cobalt blue, h 275	on the wheel: burnt sienna, h 40	opposite hue 95: green gold, h 104	mixes to gray: burnt sienna, h 40 $C^* 4$ 55:45
green: permanent green light, h 159	on the wheel: pyrrole red, h 14	opposite hue 339: quinacridone magenta, h 342	mixes to gray: quinacridone magenta, h 342 $C^* 1$ 60:40

Figure 33: Three complements of six paints. Each row starts with the paint’s tint at a lightness of 60, then gives its complement on the artists’ wheel, shown as the paint standing for the opposite name; its visual complement, the calibrated paint nearest to the hue exactly opposite; and its mixing complement, the calibrated paint that brings it nearest to gray at the same lightness, with the gray it makes and the proportion by weight.

yellow is warm and a yellow-green cool. Under Itten’s a lemon yellow is nearer the cool pole than cadmium orange is. Under color temperature the warmest hue is a yellow-orange and the coolest a violet-blue, and a blue-green is neither.

Within a hue the words are relative, a cool red being one nearer violet than some other red. The split-primary palette uses them in this relative sense, so that its warm yellow is the one nearer orange and its cool blue the one nearer green, which is the bias rule tested above.

The second difficulty, in panel (b), is that the hue of a paint moves as white is added, for the reasons Sections 3.3 and 3.7 gave. Pyrrole red, an orange-leaning warm red straight from the tube, becomes a cool rose pink in a pale tint. Ultramarine, cobalt blue and phthalo blue all start as violet-blues in masstone and end as greener blues, phthalo blue as a green-blue. The usual split calls that cool to cool, while Itten’s axis calls it a move toward the cool pole and the relative usage a move from a warm blue to a cool one. Phthalo green goes from a blue-green to a green, and the two yellows move toward green as well. White brings back first the light a paint absorbs least (Section 3.7). For most paints that light lies on the cool side, so most paints cool as they are tinted, but the earths and green gold do not. The warmth of a paint has to be stated at a lightness to mean anything.

None of this makes the associations unreal. Warm and cool are tied to fire and sunlight on one side and to water, shade and distance on the other [37]. The blue of distant hills is a physical

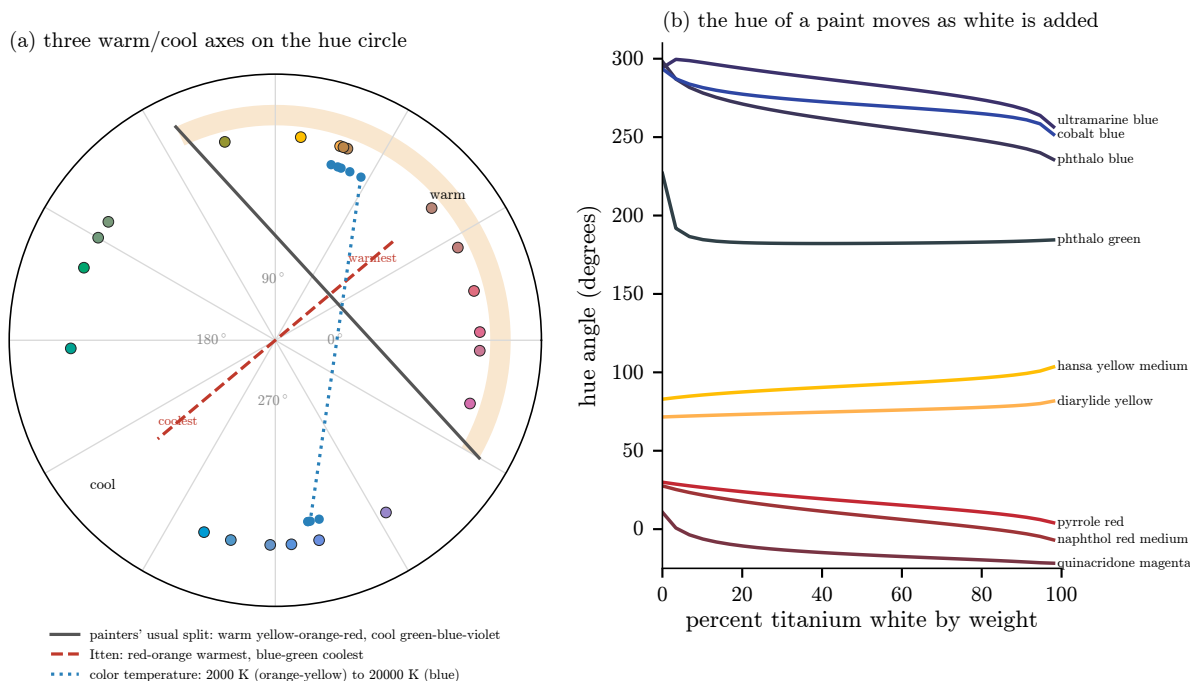


Figure 34: Warm and cool. (a) The calibrated paints' tints at a lightness of 60 on the measured hue circle, with three warm-cool axes: the painters' usual split, Itten's axis from red-orange to blue-green [37], and the colors of a glowing body heated from 2000 to 20000 kelvin, drawn relative to daylight. (b) The hue angle of nine paints as titanium white is added by weight: the reds move toward violet, the blues toward green, the yellows toward green.

fact, the scattering of short wavelengths by the air, so the landscape painter's rule that cool colors recede rests on something. The words do not, though, describe a measurable property of a pigment. Neither the eye's color channels nor CIELAB nor Munsell has a direction that corresponds to warmth, and the Natural Color System, which was built from judgments of hue resemblance alone, found no need for one [29].

The nearest thing to a physical meaning is color temperature, and its line runs within thirty degrees of CIELAB's yellow-blue axis, the eye's yellow-blue channel. If warmth is anything measurable, it is how far a color sits toward yellow and away from blue. By that measure a lemon yellow is as warm as an orange, a magenta is cool, and a green and a red that sit equally far toward yellow are equally warm. That is not what the painter's rule says, which is a fair sign that the rule is about something other than measurement. For mixing it is the bias rule again, and Section 4.5 has already given the verdict on that.

4.9. The masstone is not the paint's color. Color charts, tube labels and most books show a paint by its masstone, the paint straight from the tube in a thick layer, and painters are taught to read a paint's hue from it. For the dark transparent paints this is wrong, and measurably so. Dioxazine purple in masstone is a near black with the faintest lean toward red, and its tint is a violet. Phthalo green's masstone has the hue of a blue and its tint the hue of a green. Phthalo blue's masstone leans toward violet and its tint toward green. These are Okumura's measurements, not the model's. A paint whose masstone has a chroma under 10 has no hue a

chart can show, and the only honest picture of it is a tint or a glaze.

For thirteen Golden paints, Figure 35 sets the measured masstone beside the lightest step of Okumura's tint ladder [59]. For the dark transparent paints the hue moves a long way between the two, as much as 57 degrees for dioxazine purple and phthalo blue. Even semi-opaque paints such as pyrrole red and cobalt blue move by 20 degrees or more, for the reasons given in Sections 3.3 and 3.7. Only the opaque, light paints hold their hue: chromium oxide and yellow ochre move by about ten degrees or less.

masstone	lightest tint	
$C^* 3, h 1$	$C^* 43, h 304$	dioxazine purple: tint is 20% paint; hue moves 57°
$C^* 8, h 234$	$C^* 38, h 185$	phthalo green (blue shade): tint is 10% paint; hue moves 49°
$C^* 25, h 300$	$C^* 36, h 244$	phthalo blue (green shade): tint is 10% paint; hue moves 57°
$C^* 8, h 309$	$C^* 32, h 269$	anthraquinone blue: tint is 20% paint; hue moves 39°
$C^* 28, h 6$	$C^* 38, h 337$	quinacridone magenta: tint is 10% paint; hue moves 28°
$C^* 18, h 16$	$C^* 33, h 355$	quinacridone crimson: tint is 20% paint; hue moves 20°
$C^* 4, h 174$	$C^* 23, h 151$	jenkins green: tint is 20% paint; hue moves 22°
$C^* 4, h 282$	$C^* 17, h 265$	paynes gray: tint is 20% paint; hue moves 17°
$C^* 25, h 299$	$C^* 34, h 276$	ultramarine blue: tint is 20% paint; hue moves 23°
$C^* 69, h 30$	$C^* 32, h 8$	pyrrole red: tint is 10% paint; hue moves 22°
$C^* 56, h 293$	$C^* 24, h 264$	cobalt blue: tint is 20% paint; hue moves 28°
$C^* 28, h 138$	$C^* 14, h 148$	chromium oxide green: tint is 20% paint; hue moves 10°
$C^* 46, h 71$	$C^* 26, h 79$	yellow ochre: tint is 20% paint; hue moves 8°

Figure 35: Masstone against tint, measured. For thirteen Golden Matte Fluid paints, the masstone and the lightest step of Okumura's tint ladder [59], each drawn in its measured color and labeled with its chroma and hue angle, with the distance the hue moves between them.

The masstone hue of a paint with a chroma of 3 or 4 means little. It is the angle of a point lying close to the gray axis, and the instrument places that point only as well as the surface floor allows (Section 2.2). Part 3 compared hues using tints at a fixed lightness for this reason, and a painter who chooses a dark transparent paint by its masstone on a chart is choosing by the wrong number.

The surface floor and the tint peak of Section 3.4 explain the difference together. A dark transparent paint in a thick layer reflects little more than the surface floor at most wavelengths. In the band it passes it differs from a black by a percent or two, and the hue those few percent define is ruled by whichever end of the spectrum leaks most. For the phthalos that is the short-wave end, so their masstone hues lie further round toward blue and violet than their tints'. Adding white lifts the passed band up the steep part of the curve that turns K/S into reflectance,

while the absorbed bands stay down, and only then does the pigment's real pattern of absorption appear as a color.

4.10. What survives. The rules that fail were made to describe colors by their look and were then asked to predict what pigments do. The eye adds up the light a surface returns in three broad, overlapping bands, one for each kind of cone, and then compares the three signals in two ways. A mixture of paints adds up its pigments' absorption and scattering one wavelength at a time, and the Kubelka–Munk law turns the sums into reflected light. The first process is behind the three kinds of cone signal, the four hues that look elementary and the circle of hues itself. The second is why a red and a blue make gray, why a dark transparent paint comes alive in a tint, why white adds a faint blue cast to a mixture, and why no three paints are enough. The rules of the wheel mix the two up. What survives of them is modest and useful: that hues form a circle; that lightness, chroma and hue are the three things to name; that a color is dulled by its mixing complement and set off by its visual one, which are often different paints; and that six well-chosen paints reach more than three. Everything beyond that is better read off the reflectance curves, which this paper has tried to show are not hard to read. A painter without an instrument can still see part of it in a paint's own tint ladder: a strip of the paint mixed with more and more white shows which way its hue moves and where its color is most vivid.

4.11. Appendix: the mathematics.

Primaries and the unmixable paints (Section 4.1). The three cone sensitivities peak near 445, 545 and 570 nm [70]. The unmixable test rests on Fact 3.2: a mixture's K/S at each wavelength lies between its ingredients' values there, so a paint is unmixable from a given set if its color lies outside what the set's mixtures reach, which is the case for any paint more chromatic than those mixtures in its own hue direction. The set is the best three of Section 4.3, hansa yellow medium, quinacridone magenta and phthalo blue, with white. Each of the fifteen other calibrated single-pigment paints with some chroma is taken at its own lightness, or tinted with white to $L^* = 45$ if it is darker, and its chroma is compared with how far the three and white reach in its hue direction at that lightness; it counts as outside if it passes that reach by more than 1.5 units. Seven are outside: diarylide yellow, with a chroma of 90 where the three reach 43; pyrrole red, 66 against 49; naphthol red medium, 54 against 47; dioxazine, 46 against 35; ultramarine, 60 against 35; cobalt blue, 52 against 35; and phthalo green, 42 against 32. Eight fall inside: the four earths, yellow ochre, raw sienna, red oxide and burnt sienna, which are dull to begin with; quinacridone crimson and chromium oxide; cerulean blue; and anthraquinone blue, which the three reach to within two units. The test is in the scripts of Figures 30 and 28.

Narrow and broad bands (Section 4.2). Lightness is the cube root of the luminance factor Y (equation (5)), and Y is the integral of the reflectance against the luminous efficiency function $\bar{y}(\lambda)$ (equation (3)), which is a bell about 100 nm wide at half height, centered on 555 nm. A band 25 nm wide near the peak catches a quarter of the area under the bell and gives $Y = 0.24$, hence $L^* = 56$. In Figure 29(a), cadmium yellow medium's luminance comes 0.3 percent from below 490 nm, 34 percent from 490 to 560 nm, 33 percent from 560 to 590 nm and 32 percent from above 590 nm. In panel (b), the band from 565 to 590 nm, the yellow of the spectrum, gives a lightness of 56, a chroma of 96 and a hue of 88°. The narrower band from 575 to 585 nm gives a lightness of 41, and widening the band to 555 to 605 nm raises it only to 70, still below any yellow paint. A surface reflecting everything above 500 nm has a lightness of 97 and a chroma of 125. The green band alone, 515 to 545 nm, has a lightness of 61 and a chroma of 154; the blue

band, 455 to 485 nm, a lightness of 23; and the red band from 620 nm up, 33. In panel (c) the lightness of a band centered on 580 nm climbs from 41 for a width of ten nanometers to 88, above cadmium yellow medium's 86, at about a hundred nanometers, which means reflecting from 530 to 630 nm; the chroma peaks at a width of about a hundred and then falls. Chroma comes from the differences between the cone signals, so a narrow band, which gives large differences, can be very chromatic while it is dark. In panel (d) the yellow band excites the L and M cones at 24 and 20 percent of their response to white, and the broad yellow at 43 and 35, while neither excites the S cones.

Regions and areas (Section 4.3). The regions of Figure 30 are drawn in the a^*b^* plane at $L^* = 40, 55$ and 70 . The region of all 26 calibrated paints follows the outermost of the mixtures of every pair of them, each brought to the lightness with white. The region of three paints is bounded by the three mixing lines between them, each mixture brought to the lightness with white, with the corner near a yellow, which is lighter than the lightness in question, replaced by the three-paint mixtures that have that lightness with no white at all. Mixtures of three paints lie inside the lines between pairs, since they sag further toward gray. Searching every set of three from fifteen chromatic calibrated paints for the largest area at $L^* = 55$ found the cyan-magenta-yellow set itself. As fractions of the area of all possible surface colors, the red-yellow-blue set and the best three cover 11 and 17 percent at $L^* = 55$, against 23 percent for all 26 paints; at $L^* = 40$ the numbers are 7 and 13 percent against 18, and at 70 they are 13 and 16 against 23. A paint whose K/S spectrum is not a positive combination of the three is unmixable from them, and a paint whose color lies outside the bent triangle is one of these. For lights, the tristimulus values of a mixture are the sums of the tristimulus values of the lights (Grassmann) [26]. Three lights match every color only if one of them may be added to the color being matched instead of to the mixture, which amounts to a negative amount of that light; with positive amounts only, mixtures fill the straight-sided triangle of the three primaries on the chromaticity diagram; since the spectrum locus is convex, no triangle inside it contains all of it, and the sRGB primaries enclose about a third of the diagram's area [78, 36].

The two sets compared (Section 4.4). Averaged over lightnesses of 30, 40, 50, 60, 70 and 80, the red-yellow-blue set hansa yellow medium, pyrrole red and ultramarine covers 9.0 percent of the area of all possible colors, and the set diarylide yellow, naphthol red medium and cobalt blue covers 6.4 percent. The set hansa yellow medium, quinacridone magenta and phthalo blue covers 13.2 percent, and diarylide yellow with the same magenta and blue 9.4 percent. The advantage of the magenta-and-phthalo sets is largest in the dark colors: at a lightness of 40 they reach 9 to 13 percent against 5 to 7, and at 30, 3 to 4 against 1 to 2. The red sets win in a narrow wedge: pyrrole red at a lightness of 45 has a chroma of 66 at 27° where the magenta set reaches 49, and ultramarine at a lightness of 45 has 60 at 293° where the magenta set reaches 35. The magenta sets win across the whole violet third and the green third of the circle: at 305° and a lightness of 45 the red set reaches a chroma of 16 against the magenta set's 35; at 349° it reaches 19 against 54; and at 183° , the hue of phthalo green, 17 against 32.

The bias test (Section 4.5). The lean of each paint is the hue angle of its tint at $L^* = 60$, or of its masstone for the yellows lighter than that: a blue whose tint leans toward green has a hue nearer 200° , one that leans toward violet nearer 280° . Each paint is mixed with a fixed partner in 201 proportions by weight, as in Section 3.8, each mixture is brought to a fixed lightness with

white, and the chroma is recorded for the proportion whose hue comes closest to a target hue, if it comes within five degrees. The partners and targets are hansa yellow medium for the blues' greens (155° , $L^* = 60$) and the reds' oranges (58° , $L^* = 65$); quinacridone magenta for the blues' violets (315° , $L^* = 45$); ultramarine for the reds' violets (315° , $L^* = 45$); phthalo blue for the yellows' greens (155° , $L^* = 60$); and pyrrole red for the yellows' oranges (58° , $L^* = 65$). For the blues, the greens are 21 to 25 for four of the five, from ultramarine at a hue of 282° to cerulean blue at 257° , and rise to 42 for phthalo blue at 250° . Cerulean gives 25 and phthalo blue, eight degrees away, 42: a difference of 17 units. The violets run from 41 for cobalt blue and 40 for ultramarine down to 37 for phthalo blue, a fall of 4 units across the whole range of blues. For the reds, the oranges are 35 for red oxide at 27° , 64 for pyrrole red at 14° , 65 for naphthol red medium at 2° , 46 for quinacridone crimson at -3° and 52 for quinacridone magenta at -18° . The violets with ultramarine are 8 for red oxide, 15 for pyrrole red, 24 for naphthol red, 19 for quinacridone crimson and 40 for quinacridone magenta. For the yellows, the greens with phthalo blue fall from 49 for green gold at 104° to 21 for diarylide yellow at 72° , and the oranges with pyrrole red rise from 40 to 76 over the same range, with the two earth yellows as the outliers at 37 and 31. By equation (21) the mixture in each band has a K/S between the parents', and a secondary is chromatic in proportion to what both parents reflect in the band that makes the secondary's hue. Cerulean and phthalo blue make different greens because phthalo reflects far more at 490 to 520 nm relative to its own total and is a far stronger and more chromatic paint.

Hue circles (Section 4.6). The paints of Figure 32(a), at the hue angles of their tints, are, going round from yellow: hansa yellow medium at 83° , green gold for yellow-green at 104° , permanent green light for green at 159° , phthalo green for blue-green at 182° , cobalt blue at 275° , ultramarine for blue-violet at 282° , dioxazine for violet at 303° , quinacridone magenta for red-violet at 342° , pyrrole red at 14° , red oxide for red-orange at 27° , burnt sienna for orange at 40° and diarylide yellow for yellow-orange at 72° . The measured steps between neighbors are 21, 55, 23, 92, 8, 20, 39, 32, 13, 13, 31 and 11 degrees, against the wheel's twelve steps of 30. The wheel's third from red to yellow spans 69 measured degrees, its third from yellow to blue 192, and its third from blue to red 99, since red, yellow and blue are at 14, 83 and 275° . The Munsell hues of panel (b) are computed from the 1943 renotation [58] at value 6 and chroma 6 under illuminant C. Munsell's ten named hues sit at measured angles of 28° (5R), 63° (5YR), 93° (5Y), 118° (5GY), 161° (5G), 188° (5BG), 227° (5B), 273° (5PB), 314° (5P) and 356° (5RP), with steps of 35, 30, 25, 43, 27, 38, 46, 41, 42 and 32 degrees, between 25 and 46 where the wheel's lie between 8 and 92.

Complements (Section 4.7). Each paint in Figure 33 is taken as its tint at $L^* = 60$. Its visual complement is the calibrated paint whose tint hue is nearest the hue 180° away, and its mixing complement the calibrated paint that, in the best proportion, brings the mixture at $L^* = 60$ nearest to gray. For hansa yellow medium, at 83° , the opposite is 263° , nearest to cerulean blue at 257° , and the mixing complement is dioxazine purple at 303° , at 59 parts yellow to 41 of dioxazine, leaving a chroma of 4. For burnt sienna, 40° , the opposite is 220° , nearest to phthalo blue, and the mixing complement is anthraquinone blue at 269° , which takes the sienna to a chroma of 0.5 at 85 to 15. For pyrrole red, 14° , the opposite is 194° , near phthalo green, and the mixing complement is permanent green light at 159° , which takes the red to a chroma of 4 at 36 to 64. For dioxazine, 303° , the opposite is 123° , and green gold at 104° is both the nearest paint to it and the mixing complement. For cobalt blue, 275° , the opposite is 95° ,

nearest to green gold, and the mixing complement is burnt sienna at 40° . For permanent green light, 159° , the opposite is 339° , and quinacridone magenta at 342° is both the nearest paint and the mixing complement, leaving a chroma of 1 against pyrrole red's 4. In the twelve-paint version of Section 3.9 the neutralizers of the blues sit 23 to 62 degrees toward red from the blues' visual opposites. In CIELAB the red-green channel is the a^* axis and the yellow-blue channel the b^* axis; pyrrole red is at 14° rather than 0° , which puts its opposite at a blue-green, and hansa yellow medium at 83° has its opposite at 263° , a blue.

Warm, cool and tints (Section 4.8). In Figure 34(a) the painters' usual boundary runs from about 115° to about 330° . Itten's axis runs from about 40° to 220° , with the boundary perpendicular to it. The line of blackbody radiators, from a candle at 2000 K to a clear sky at 20000 K, plotted as colors against daylight, runs from a hue of 62° to one of 281° [78], 20 to 60 degrees away from Itten's axis at both ends, and within thirty degrees of the b^* axis; if warmth is anything measurable, it is b^* . The lemon yellow and yellow-green of the main text are at 96° and 120° . In panel (b), pyrrole red goes from 30° in masstone to 4° at 98 percent white, and naphthol red medium from 28° to -7° . Ultramarine goes from 294° to 257° , cobalt blue from 294° to 252° and phthalo blue from 298° to 236° . Phthalo green goes from 227° to 185° . Diarylide yellow goes from 72° to 82° and hansa yellow medium from 83° to 103° .

Masstone and tint hues (Section 4.9). In Okumura's measurements [59], dioxazine purple in masstone has a chroma of 3 and a hue angle of 1° , and its tint a hue of 304° . Phthalo green's masstone hue is 234° and its tint's 185° ; phthalo blue's masstone is at 300° and its tint at 244° . Between masstone and lightest tint the hue moves by 57° for dioxazine purple and for phthalo blue, 49° for phthalo green, 39° for anthraquinone blue and 28° for quinacridone magenta. The semi-opaque paints move by 20 to 28 degrees, pyrrole red from 30° to 8° and cobalt blue from 293° to 265° . Chromium oxide moves 10° and yellow ochre 8° .

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