# Chapter 13
# Measurement of the Optical Properties of Paints and Plastics

## Contents






M. Diebold et al., *Pigments, Extenders, and Particles in Surface Coatings and Plastics*, https://doi.org/10.1007/978-3-030-99083-1_13

## Introduction

There are three fates for light entering a paint film. It can pass through the film, allowing it to interact with the substrate, it can be redirected out of the film through light scattering, and it can be absorbed within the film. The balance between these fates in any given film is a function of three distances—the distance from the film surface to the substrate, the distance the light travels before being redirected out of the film, and the distance the light travels before being absorbed by a film component. The first of these distances is determined by the amount of the film applied to the substrate and the second two are determined mainly by the type and amounts of pigments, both white and color, within the film.

For complete opacity, the film thickness should be much greater than the distance the light travels before being redirected out of the film or being absorbed within it. Measuring these various distances provides us with a means by which we can quantify opacity. While we can measure film thickness directly, it is more difficult to measure the other two distances. However, we do not need to directly measure the exact values of these distances and can instead use indirect means to characterize them in a meaningful way.

There are several ways of measuring the average distance that light travels in a paint film, and therefore the number of light interactions within it. Four of these will be described in this chapter:

- contrast ratio, where distance is characterized based on the amount of light that travels through the film and strikes the substrate,
- spread rate, where reflectance values from films too thin to be opaque are used to calculate the area that a given volume of paint can cover at the full hide,
- tinting strength, where the distance light travels through an opaque film is determined by measuring the amount of light absorbed within the film (this can be used to characterize both the strength of $TiO_2$ light scattering and the strength of color pigment light absorption), and
- undertone, where differences in scattering distances (and so, in scattering strength) as a function of wavelength are determined by partially absorbing light as it travels through a mix of black pigment and titanium dioxide.

We will review each of these in turn, beginning with the contrast ratio.

## Contrast Ratio

Contrast ratio is perhaps the most common way of measuring opacity in the paint industry. This is for a number of reasons, including the ease of performing the test (one drawdown, two reflectance measurements), the intuitive nature of the measurement, and the ability to see differences among paints by eye. However, the test has several limitations, some that are commonly known and others that often go unrecognized.

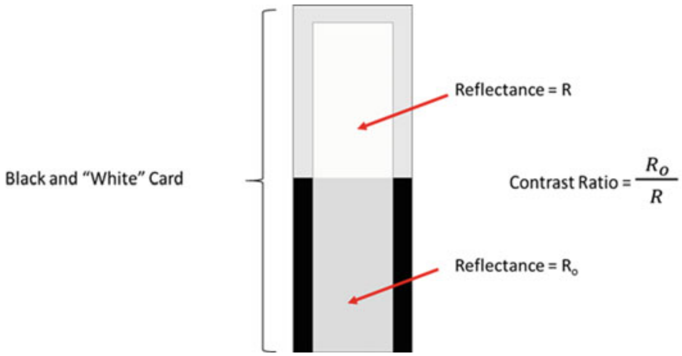



**Fig. 13.1** Definition of contrast ratio

## *Concept*

The strategy behind the contrast ratio test is straightforward. The paint of interest is drawn down on a black and white substrate (typically a paper card specially coated for this purpose).[1] After drying, the amounts of light reflected from the two areas of the card are measured (typically as tristimulus Y) and compared by taking the ratio of light reflected from the black section of the substrate ($R_o$ or "R naught") to that reflected from the white section of the substrate (R), as shown in Fig. 13.1. The contrast ratio can be reported either as a fraction (0 to 1) or a percentage (0% to 100%).

The difference in light reflectance between these areas is due to light that penetrates the entire film depth and then is either absorbed by the substrate (black area) or reflected by it (white area). The contrast ratio test measures the amount of light that penetrates at least a certain distance through the film (that distance being the thickness of the film).

For this test to be accurate, the film thickness should not be so great as to give complete opacity (defined as a contrast ratio of 0.98). In such a case, so little light travels the entire distance of the film depth that it is difficult to accurately measure that amount. Nor should the film be so thin that very little light is scattered by it. The ideal film thickness is one that gives a contrast ratio between 0.92 and 0.95.[2] Often an unknown paint is applied at a series of different thicknesses to determine the most appropriate thickness for that paint to be tested.

Contrast ratio can also be measured on plastic films by placing them over a black and white chart and measuring reflectance over each area. In this case, a thin layer of oil must be applied to the chart, the film placed onto the oil, and all bubbles removed. This is necessary to prevent light from being scattered by the air gap at the plastic / chart interface. Since oil has roughly the same refractive index as the plastic film,

---

[1] The reflectance of the white portion is 0.80, making it light gray in color. However, we will follow the convention of the industry in referring to this as white.

[2] Note that ASTM D2805 specifies a somewhat higher contrast ratio target of 0.97.

light passing between the two is unperturbed. This process is known as bringing the plastic film into optical contact with the opacity chart.

## *Limitations*

While this test is simple, both in concept and practice, it does make several crucial assumptions that are often violated without recognition by the tester, and it can be used in a misleading way to minimize opacity differences that may be important in actual end-use applications. The most important of these assumptions is that the film thickness is the same for all paints being tested. This is because contrast ratio is not solely a property of the paint itself but is also a property of the drawdown thickness. Obviously, a thicker film will have a higher contrast ratio than a thinner film of the same paint.

The requirement for a constant film thickness is often addressed by using the same drawdown blade for all paints. In cases where accuracy is critical, two paints will often be drawn down side-by-side on the same drawdown card. In this way, any inaccuracies due to variability in the speed at which the paint is drawn down or due to variability in drying conditions of the paint film are thought to be avoided. In addition, this facilitates direct comparison by eye between the paints.

Unfortunately, the situation is more complex than this. It is commonly believed in the coatings industry that the wet film thickness of a drawdown is determined only by the gap in the drawdown blade and that this thickness is equal to the drawdown clearance. Neither of these beliefs is correct. The actual wet film thickness of a drawdown is, in fact, roughly half the gap clearance. This would be of little consequence if that thickness was identical for all paints, but this is not the case. The rheology of the paint has a strong effect on the wet film thickness, with more viscous paints giving a thicker wet film than less viscous paints.[3]

As an indicator of how widely the wet film thickness can vary from one paint to another, we show in Fig. 13.2 a histogram of the wet film thicknesses of 246 similar paints (differing only in the relative amounts of extender and $TiO_2$ pigment) drawn down by an automated draw down apparatus using the same blade for all drawdowns. For these paints, the wet film thicknesses were between 67.0 and 86.6 microns, a range of 22%. Since total scattering (SX) is equally sensitive to scattering strength (S) and film thickness (X), a 22% variation in film thickness would be interpreted

[3] This can explain why adding nanoparticle extenders to some paints can seemingly improve opacity. The mechanism claimed for these opacity improvements is better spacing of the $TiO_2$ particles, which would increase their scattering efficiencies. However, small particles are known to increase the viscosity of paints (and are often used for this purpose), and if the paint viscosity after nanoparticle addition is not adjusted to the original viscosity, then a thicker drawdown can result. Of course, such an increase in thickness will increase the opacity of the film, but not because of better $TiO_2$ particle spacing. On a spread rate or coverage basis (square meters per liter of paint at complete opacity), there is no improvement in opacity.

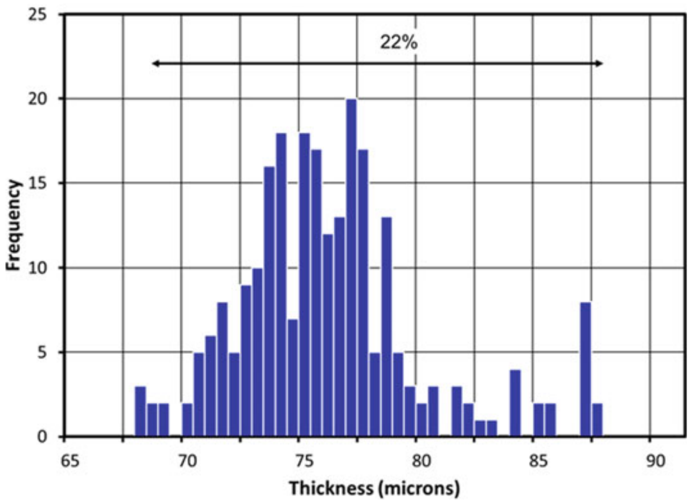



**Fig. 13.2** Histogram of the wet film thicknesses of 246 similar paints

as a 22% variation in light scattering strength if we were to assume that all film thicknesses were the same.

A second issue with contrast ratio is that while it is determined by paint opacity, it cannot distinguish between opacity due to light scattering and that due to light absorption. Two paints may have the same contrast ratio, but different brightnesses. This is illustrated in Fig. 13.3, which shows a comparison of two films with identical contrast ratios but different brightnesses. We may conclude that the performances of the two paints are identical, since the contrast ratios are the same, but such a comparison is invalid since the paints look different. Consumers don't simply desire high hiding, they desire high hiding with the specific color of their choice. As such, comparing the performance of paints with different colors (or brightnesses) is not relevant. If hiding efficiency were the only criteria for choosing a paint, then all paints would be black. This is, of course, not acceptable for most applications.

A third shortcoming of the contrast ratio test is that while one can quantify differences between the hiding abilities of different paints, these results do not give guidance as to how to change the paint film to achieve a certain level of improvement. That is, one paint film may be shown to be less opaque than another under certain application conditions, but the contrast ratio provides no quantitative information as to how much the opacity properties of the lower opacity film must be changed to equal the other film. For example, we do not learn from contrast ratio how much thicker a film must be made to achieve complete opacity, or how much stronger either the light absorption or the light scattering must be made to do so (or what combination of the two will give complete opacity).

A final problem with the contrast ratio test is that it is prone to either intentional or unintentional misuse. There is a truism that any paint or plastic film can be opaque as long as the film is thick enough. If we are comparing the opacity of a low-quality

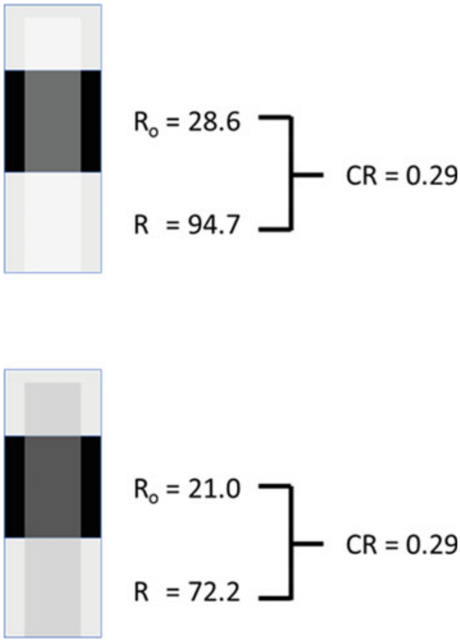



**Fig. 13.3** Two paint films with the same contrast ratio. The brightness ($R_\infty$, discussed below) of the top paint is 0.96 while that of the bottom paint is 0.67

paint to that of a high-quality paint, we might find that the two are equally opaque after six coats are applied. However, this is of no relevance to the paint consumer, who is expecting complete opacity with a single or, at most, double coating of the paint. At these lower film thicknesses, there is likely to be a significant difference in opacity between the high- and low-quality paints.

This is relevant to the contrast ratio test because the contrast ratio of two films can be close to one another even if the true opacities of the two paints, measured, for example, as square meters covered per liter of paint, are quite different. This occurs when the paints are applied too thickly. As an example, Table 13.1 shows the contrast ratios reported in an extender advertisement for a series of paints for which some of the $TiO_2$ is replaced with the advertised extender. We see that the contrast ratio of the reference paint, at 0.997, is only slightly higher than the contrast ratio of the paint made with a 10% replacement of $TiO_2$ (0.993). Such a difference in contrast ratio would be impossible to see by eye, suggesting that the opacities of the two paints are functionally equivalent.

However, it is clear from the contrast ratio values that these paints were applied at a much greater thickness than is needed for complete opacity. While the difference

**Table 13.1** Contrast ratio measurements on two paints

| % $TiO_2$ replacement | Contrast ratio |
|---|---|
| Reference | 0.997 |
| 10% | 0.993 |

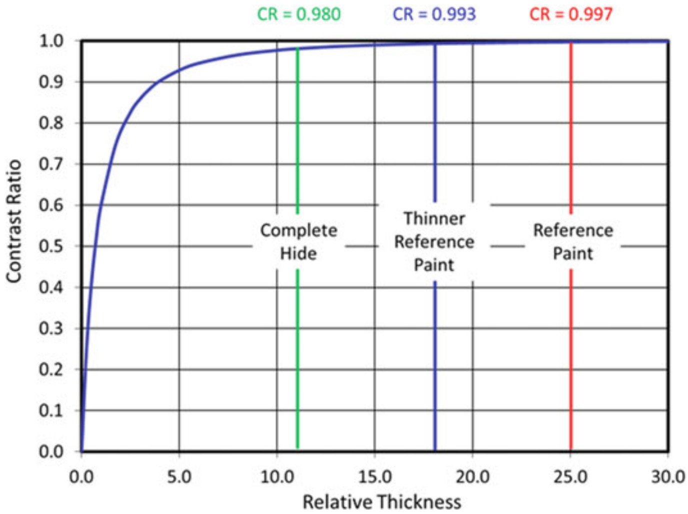



**Fig. 13.4** Contrast ratio as a function of relative film thickness for a white paint

in contrast ratios between complete hide (0.980) and measured hide for the reference paint as applied (0.997) is less than 2.0%, the applied film was more than double the thickness needed for complete hide (see below).

We can see this in Fig. 13.4. Here, we plot the calculated contrast ratio of a white paint as a function of film thickness (blue curve).[4] On this chart, we locate the original drawdown contrast ratio with a red line and see that the relative thickness is 25 units. The location of the modified paint, with a contrast ratio of 0.993, is shown with a blue line. We would achieve the same contrast ratio—0.993—by applying the reference paint at a relative thickness of 18 units. That is, we could either reduce cost by replacing 10% of the $TiO_2$ with the special extender, or by applying a film that is 28% thinner, reducing the entire cost of coverage by 28%. These two options give identical contrast ratios. To complete our analysis, we note that a relative film thickness of only 11 units (44% of the actual thickness used) is needed to provide a complete hide for the reference paint. Even this is too thick for a valid contrast ratio test—as mentioned above, the ideal thickness for this test is one that gives a contrast ratio between 0.92 and 0.95.

## Spread Rate

The various limitations of the contrast ratio test, as outlined above, can be remedied in a straightforward manner by adding two steps to the analysis of the paint drawdown. The first is to measure the thickness of the wet film, and the second is to make

[4] An $R_\infty$ value of 0.95 was used to generate this graph.

additional computations beyond simply taking the ratio of two reflectances. These additional computations are complex, but they are easily amenable to incorporation into a spreadsheet or other program, allowing them to be automatically calculated from the properties of the drawdown.

The additional information gained from this procedure, described below, is twofold: first, we can calculate the spread rate of the paint, which is defined as the area covered at full hide by a certain volume of paint, typically reported in $m^2/l$ or $ft^2$/gallon. These values were used in Chap. 4 to quantify the scattering strength of $TiO_2$ particles in white paints (where light absorption is negligible). Second, we can calculate the expected change in spread rate if we were to modify the paint by changing its scattering and/or the absorption strengths.

Before describing the calculations involved in this procedure, we will outline the steps we will follow:

1. Paint is applied to a black and white card at a thickness that gives a contrast ratio between 0.90 and 0.95.
2. The weight of the wet paint and the area it covers are determined.
3. Based on the weight of wet paint, the area it covers, and the density of the wet paint, the volume of paint applied and the wet thickness of the film are calculated.
4. Using the volume of paint applied and the area covered, the application rate of the drawdown is calculated (this is the area that a unit volume of paint, such as one liter, will cover at the same thickness as the drawdown).
5. Reflectance over the black and white portions of the card is measured and the contrast ratio is calculated.
6. These parameters are then entered into equations that are then solved to give the spread rate of the paint (the area that a unit volume of paint will cover at complete hide, defined as a contrast ratio of 0.98), as well as the absorption and scattering strengths of the paint (abbreviated as K and S).

## *Kubelka–Munk Framework*

In Chap. 3, we described the theoretical scattering power of a single, isolated particle surrounded by either air or resin (this was termed “Mie scattering”). However, in Chap. 4, we saw that scattering efficiency is significantly decreased when other particles are nearby (this was termed “dependent scattering”). To demonstrate this effect, in that chapter we showed the measured light scattering strengths of white paints (i.e., paints for which light scattering was much stronger than light absorption) as a function of a number of paint parameters. We did not, however, describe how these scattering strengths were measured. Separately, in Chap. 8, we discussed the ability of color pigment particles to absorb visible light. In that discussion, we considered the effects of the intrinsic absorption strength of the material, its concentration, and its thickness on the total amount of light absorbed.

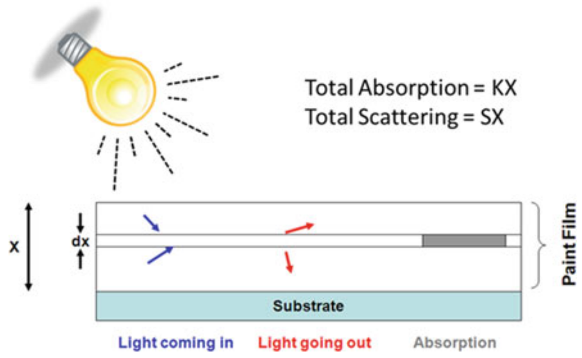



**Fig. 13.5** The Kubelka–Munk model. The total film thickness is X and the thickness of a thin layer is dX

Although we have so far considered light scattering and light absorption separately, in nearly all paints, (and plastics) both occur together, and it is their combination that determines opacity. In the 1930s, German physicists Paul Kubelka and Franz Munk developed a system for measuring light absorption and light scattering simultaneously in a paint film [1]. Their approach was to ignore the fact that both of these processes involve interactions with individual particles and instead treat them as intrinsic properties of a volume of paint film.

By making this simplifying assumption, Kubelka and Munk derived a series of powerful equations that describe the optical properties of a paint. These equations can be used to calculate the light scattering and light absorption strengths of a paint, the opacity of any thickness of that paint (or, conversely, the film thickness required for any desired opacity), and the effect of changing the light scattering or light absorption strengths on paint opacity. In addition, these equations can be used to calculate the color resulting from mixtures of individual colorants or paints (this will be discussed in detail in Chap. 15).

The Kubelka–Munk approach is based on an accounting of the amount of light entering and exiting a thin layer within a paint film over a short period of time (Fig. 13.5) [2]. During this time, light will enter this thin layer both through the lower boundary of the layer (light moving toward the substrate) and the upper boundary of the layer (light moving toward the film surface). This is shown by the blue arrows in Fig. 13.5. Similarly, some light will exit this layer through both the upper and lower boundaries (the red arrows in Fig. 13.5), and, finally, some light within the layer will be absorbed (the gray region in Fig. 13.5).

Kubelka and Munk were able to model the interactions between the paint film and light by making some simplifying assumptions. These are that the light striking and within the film is diffuse (that is, the intensity of light traveling in every direction is the same), that there are no special interactions (such as reflection) at the film/air and film/substrate interfaces, that the film is homogenous (which ignores that it is discrete particles that interact with light), that these particles are evenly distributed throughout the film, and that the film thickness is much greater than the thin layer thickness.

These assumptions are not true for every paint film, and it must be emphasized that the results of the Kubelka–Munk analysis are only as sound as the assumptions going into them. For example, the light striking a paint is rarely diffuse. In addition, very thin paint films might not be thick enough for the light to randomize. Similarly, in very dark films, all of the light could be absorbed before it is randomized. Moreover, a significant amount of light can reflect from the film surface, both as the light enters the film and as it exits the film. Despite the limitations of these assumptions, the Kubelka–Munk analysis of most paint films is valid, at least for comparison purposes.

### *Application of the Kubelka–Munk Equations to Spread Rate*

The general procedure for using the Kubelka–Munk equations to determine opacity and spread rate is given in ASTM and DIN specifications [3, 4]. Here, we will describe the underlying basis of these procedures.

The Kubelka–Munk assumptions described above lead to a set of differential equations. There are two ways of approaches for solving these equations, an exponential approach [1] and a hyperbolic approach [5]. The two approaches each result in several mathematical equations relating reflectance, film thickness, light absorption, and light scattering. For the practical application of this model to paint opacity and hiding power, we use the hyperbolic approach and many of the equations derived from it.

## Application Rate as Drawdown

The starting point for using the Kubelka–Munk equations to calculate the spread rate of a paint at complete hide is to draw a paint down at a thickness with incomplete hide on a black and white chart. This thickness is chosen to give a contrast ratio in the range of 0.90 to 0.95. In addition to measuring the reflectance values over the black and white portions of the card after the paint dries, we also must determine the coverage, or application rate, of the paint at the thickness it is drawn down. Application rate is defined as the area covered by a unit volume of paint. This is typically given in units of $m^2$/l or $ft^2$/gallon. Note that the application rate is a function entirely of the drawdown and is not a property of the paint itself.

To calculate the application rate, we must first determine the volume of the wet paint and the area that this volume covers. We determine the volume of the film using the weight of the film and the density of the paint (which must be either measured separately or determined based on the paint composition). We measure the area covered by this volume of paint with a ruler, after the paint has dried.

From the density of the liquid paint and the weight of the wet paint applied to the panel, we can easily calculate its volume in ml:

$$\text{ml paint} = \left(\frac{\text{paint weight}(g)}{\text{paint density}(g/ml)}\right) \quad (13.1)$$

$$\text{ml paint} = 8.3454x\left(\frac{\text{paint weight}(g)}{\text{paint density}(lb/gal)}\right) \quad (13.2)$$

The thickness of the wet paint, in microns or in mils (thousandths of an inch), is

$$X(\text{micron}) = 10,000x\left(\frac{\text{volume paint }(ml)}{\text{area(square cm)}}\right) \quad (13.3)$$

$$X(mil) = 61.0273x\left(\frac{\text{volume paint}(ml)}{\text{area(square inches)}}\right)$$

$$X(mil) = 61.0273x\left(\frac{\text{volume paint}(ml)}{\text{area (square inches)}}\right) \quad (13.4)$$

Finally, we can calculate the application rate of the drawdown as follows:

$$\text{Application Rate}\left(m^2/l\right) = 0.1x\left(\frac{\text{area (square centimeters)}}{\text{paint weight}(g)/\text{paint density}(g/ml)}\right) \quad (13.5)$$

$$\text{Application Rate}\left(ft^2/gal\right) = 3.15x \left(\frac{\text{area(square inches)}}{\text{paint weight}(g)/\text{paint density}(lb/gal)}\right) \quad (13.6)$$

In these equations, a lower case “x” indicates multiplication while an upper case “X” is film thickness.

## Calculation of SX and KX

The next step in determining the spread rate of a paint is to measure the reflectance values of the dry paint over the two portions of the drawdown card. From these reflectances, we can calculate the total absorption and scattering strengths, KX and SX, by using two secondary, or “helper”, parameters, *a* and *b*:

$$a = \frac{1}{2}\left[\mathrm{R} + \frac{\mathrm{R_o} - \mathrm{R} + \mathrm{R_g}}{\mathrm{R_o R_g}}\right] \quad (13.7)$$

where

R = reflectance over the white part of the drawdown card,

$\mathrm{R_o}$ = reflectance over the black part of the drawdown card, and

$R_g$ = reflectance of the white part of the card before application of the paint

$$b = \sqrt{a^2 - 1} \tag{13.8}$$

In Chap. 6, we measured R at each wavelength interval to characterize the absorption spectrum (and color) of a paint (this was done at complete hide; that is, we measured $R_\infty$, as described below, at each wavelength interval). In Eq. 13.7 and those that follow, the R value represents reflectance over the entire visible spectrum and is typically measured as the tristimulus Y value of the paint at full hide.

In Eq. 13.7, $R_g$ refers to the reflectance of the white portion of the drawdown card prior to paint application. It is useful that some light be absorbed by the "white" portion of this card as this will allow the amount of light that passes through the paint film to the substrate to be calculated. The value of $R_g$ for standard drawdown cards is 0.80. However, there can be variability from this value, and it is recommended that the $R_g$ for each card be measured at six locations prior to draw down and that the average of these reflectances be used in these equations.

We can calculate the value of SX as a function of *a*, *b* and the reflectance over the black portion of the card ($R_o$) as follows:

$$SX = \frac{1}{b}\mathrm{Arctgh}\left[\frac{1 - aR_o}{bR_o}\right] \tag{13.9}$$

where "Arctgh" is the hyperbolic arc-cotangent function ($\coth^{-1}$).

We can calculate KX as

$$KX = SX(a - 1) \tag{13.10}$$

## Reflectance of a Film at "Infinite" Thickness—$R_\infty$

Before moving to the calculation of spread rate, it is helpful to introduce the concept of $R_\infty$ and the very useful diagram developed by Deane Judd, a pioneer in paint optics, in 1937 [6]. This diagram was developed prior to the ready availability of calculators and computers to graphically estimate the solutions of the Kubelka–Munk equations, greatly reducing the amount of work necessary to calculate the K, S, and spread rate properties of a paint.

To define $R_\infty$, we begin by imagining a series of drawdowns of the same paint at different film thicknesses onto black and white cards. For the thinner films, we are able to see a difference in reflectance over the two parts of the card. As the film becomes thicker, the magnitude of this difference decreases until, at some point, the two areas of the cards appear the same ($R_o$ = R). We refer to this reflectance as $R_\infty$

("R infinity") and define the thickness for this drawdown as $X_\infty$ ("X infinity"). Note that not only do the two areas of the film appear identical, but any film drawn down at a greater thickness will appear the same as the film drawn down at $X_\infty$.

The physical implication of $X_\infty$ is that all of the light entering a film of this thickness or greater is either reflected back out of the film or is absorbed by components of it before it reaches the substrate. Since no light reaches the substrate, the appearance of the film over any the substrate will look the same. The reflectance at a thickness of $X_\infty$ or above ($R_\infty$) is determined by the balance between the light absorption (K) and light scattering (S) within the film. Obviously, when the ratio K/S is high, the film is dark, while when it is low, the film is light. For this reason, the $R_\infty$ value is often referred to as the brightness or reflectivity of the film.

The relationship between K, S, and $R_\infty$ is given by Eq. 13.11:

$$R_\infty = 1 + \frac{K}{S} - \sqrt{\left(\frac{k^2}{S^2}\right) + 2\frac{K}{S}} \tag{13.11}$$

This equation can be rearranged to give perhaps the most widely known of the Kubelka–Munk equations:

$$\frac{K}{S} = \frac{(R_\infty - 1)^2}{2R_\infty} \tag{13.12}$$

It is impossible to ensure that every photon that enters a film does not pass through it and strike the substrate, regardless of how thick that film is. $R_\infty$ is therefore a value that can be approached asymptotically but never quite achieved. Because of this, no paint can have a truly complete hide. However, by long-established convention, a paint is considered to have a complete hide when its contrast ratio is 0.98 (or above) [7]. This value was chosen based on the ability of the average human eye to discern a difference in reflectance between the paint over the white section of the card and the paint over the black section. By definition, a film that has a contrast ratio of 0.98 or above is infinitely thick.

Like S and K, $R_\infty$ is a fundamental property of the paint itself and not of any particular drawdown. That is, while the R and $R_o$ reflectances of paint drawndowns will vary with film thickness, the $R_\infty$ value is the same for all drawdowns, regardless of thickness, of that paint.

## The Judd Graph

While the intention of this chapter is to show how the opacity properties of a paint film can be calculated based on that film's optical properties, it is worthwhile at this juncture to consider a very useful graphical approach to this problem, the so-called Judd Graph. This graph is shown in Fig. 13.6. Here, we plot two easily measured

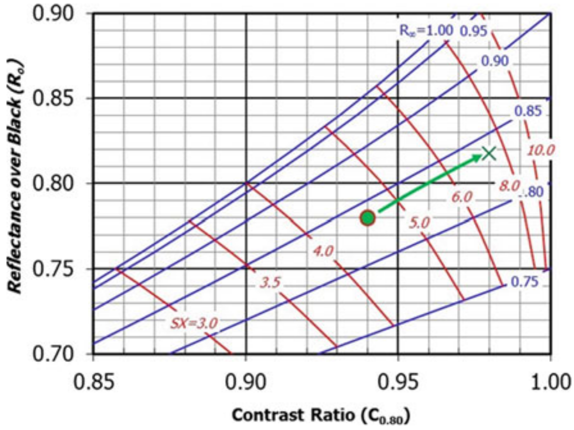



**Fig. 13.6** Judd Graph relating $C_r$ and $R_o$ to SX and $R_\infty$. The $R_g$ value is 0.80 (as indicated by the designation "$C_{0.80}$" on the X-axis)

film properties—$R_o$ on the Y-axis and contrast ratio on the X-axis—and read from the graph two properties that are difficult to calculate, at least by hand—SX and $R_\infty$.

As an example, consider a paint drawdown that has a $R_o$ value of 0.78 and an R value of 0.83 on a card with a white background reflectance value ($R_g$) of 0.80. From these reflectance values, we calculate the contrast ratio to be 0.94 (0.78/0.83). Using the black rectilinear lines in Fig. 13.6, we place this drawdown information on the graph as a green circle. We can estimate the SX value of this film using the family of red curves as a guide. This value is between 4.0 and 5.0, and closer to 5.0, and we might estimate it to be 4.6. Likewise, the $R_\infty$ value can be estimated using the family of blue lines, and here we see the data point lies between $R_\infty$ values of 0.80 and 0.85, and we might estimate it to be 0.84.

Drawdowns of the same paint at other thicknesses will all have the same $R_\infty$ value as this drawdown (recall $R_\infty$ is a property of a paint, not of a drawdown), but different SX values (because the X values are different, SX is a property of the drawdown rather than the paint). Because the SX values are different, these drawdowns will appear at different locations along the same $R_\infty$ line.

We can use this graph to estimate the spread rate of this paint at the complete hide. We do this by following the $R_\infty$ line up and to the right, until it intersects the vertical line at a contrast ratio of 0.98 (this is shown by a green arrow in Fig. 13.6). At the intersection point (green X in this figure), we use the red SX curves to estimate an SX value at the complete hide. Here, we might estimate it to be 7.5.

Before proceeding, note that the Judd Graph shown in Fig. 13.6 is calculated based on an $R_g$ value of 0.80. $R_g$ values of actual drawdown cards may vary somewhat from this value, but if the $R_g$ value is close to 0.80, this version of the Judd Graph can be used.

Since the original drawdown and the hypothetical drawdown at a contrast ratio of 0.98 (full hide) are made with the same paint, they must have the same S value (recall S is a property of a paint rather than of a specific drawdown). Thus, the difference in SX values between the drawdown (4.6) and the estimate of the paint at complete hide (7.5) is entirely due to the difference in film thickness (X). If we determined, using Eq. 13.6, that the application rate of the film as drawn down (green circle in Fig. 13.6) is 12.80 $m^2$/l, then the spread rate at complete hide is this value times the ratio of X values (4.6/7.5), or 7.85 $m^2$/l.

The historical importance of the Judd Graph is difficult to overstate. When Kubelka and Munk first published their work, it was not immediately embraced by the coatings industry [6]. This was not because the coatings industry did not think the analysis was useful, but rather because the equations involved are so complex and their solutions are far from simple to calculate, particularly with the computational tools available at the time. The effort needed to solve Eqs. 13.9–13.12 was far too great to allow them to be useful in, for example, quality control. Instead, their use was mainly limited to fundamental and applied research labs. By deriving a graphical solution to these complex equations, SX and $R_\infty$ could be determined in seconds.

Today we can quickly and accurately solve complex mathematical equations using calculators and computers and so no longer rely on the Judd Graph. That said, this graph continues to be very useful in mapping out the performance attributes of paints and in visualizing complex relationships between paints, and this diagram still has an important place in coatings science.

## Calculation of Spread Rate

In the previous section, we graphically estimated the spread rate of a paint at complete hide by using the Judd Graph to estimate the SX and $R_\infty$ value of a film drawn down at incomplete hide and then extrapolating these values to other drawdown thicknesses. In this section, we derive the equations that perform this task exactly, rather than estimate it graphically.

Our solution uses the application rate as drawndown and the R and $R_o$ values of the drawdown. We begin by solving for SX using Eq. 13.9. While it is not apparent from Eq. 13.7, *a* is a property of the paint, rather than of a drawdown. The same is true for *b*. This can be seen in these alternative equations for *a* and *b* that are based on other parameters that are properties of the paint:

$$a = \frac{1}{2}\left(\frac{1}{R_\infty} + R_\infty\right) \tag{13.13}$$

$$b = \frac{1}{2}\left(\frac{1}{R_\infty} - R_\infty\right) \tag{13.14}$$

$$a - b = R_\infty \tag{13.15}$$

$$a + b = \frac{1}{R_\infty} \tag{13.16}$$

$$a = \left(\frac{S + K}{S}\right) \tag{13.17}$$

Using the definition of contrast ratio, $C_r$ ($C_r = R_o/R$), we can substitute $R_o$ with $C_r$ times R in Eq. 13.7 and rearrange to get:

$$C_r R_g R^2 + \left(C_r - 2aC_r R_g - 1\right)R + R_g = 0 \tag{13.18}$$

Before proceeding, we must address the issue of which value of $R_g$ we should use in this (and subsequent) equations. It is important to use the measured $R_g$ value when calculating $a$ in Eq. 13.7 so as to obtain the most accurate value of SX of the film (Eq. 13.9). However, moving forward we will be *calculating* the appearances of drawdowns, rather than measuring them. When doing so, it is critical that a common $R_g$ value be used in all calculations, since the contrast ratio of a drawdown is affected by the $R_g$ value. In theory, we could choose any value for $R_g$ between 0 and 1, but for our purposes, we will use a value of 0.80, since this is the value Judd used in his graph and is typical of drawdown cards.

Returning to Eq. 13.18: The $a$ parameter is constant for a given paint, and $R_g$ is assigned a value of 0.80, for the reasons discussed above. If we specify a value for $C_r$ (typically 0.98, the condition of complete hide), then R is the only unknown. As written, Eq. 13.18 is a simple quadradic for R. We solve this using the standard procedure to give

$$R = \frac{-\left(C_r - 2aC_r R_g - 1\right) \pm \sqrt{\left(C_r - 2aC_r R_g - 1\right)^2 - 4C_r {R_g}^2}}{2C_r R_g} \tag{13.19}$$

There are two solutions for R. The equation using the positive root gives an R value greater than 1, which is physically impossible (such a condition requires more light to be reflected than actually strikes the film). We therefore use the negative root of this equation to find R at complete hide:

$$R = \frac{-\left(C_r - 2aC_r R_g - 1\right) - \sqrt{\left(C_r - 2aC_r R_g - 1\right)^2 - 4C_r {R_g}^2}}{2C_r R_g} \tag{13.20}$$

With R in hand, it is trivial to calculate $R_o$ at complete hide using the definition of contrast ratio ($R_o = RC_r$). This allows us to calculate the SX value at complete hide using Eq. 13.9, since we now know $a$, $b$, and $R_o$.

Assuming the contrast ratio of the drawdown is between 0.90 and 0.95, which is the target contrast ratio for this analysis, the SX values as drawndown and at complete hide are different from one another. Since S is constant, the X values must be different. We calculate the spread rate at complete hide by multiplying the application rate as drawndown by the ratio of SX values:

**Table 13.2** Comparison of estimated and calculated spread rates

| Quantity | Estimated from the Judd Graph | Calculated | Equation used |
|---|---|---|---|
| SX as drawn down | 4.6 | 4.562 | Equations 13.7, 13.8, 13.9 |
| $R_\infty$ | 0.84 | 0.837 | Equation 13.11 |
| Application rate as drawn down | – given as 12.80 $m^2/l$ – | | |
| SX at complete hide | 7.5 | 7.326 | Equations 13.7, 13.8, 13.9 |
| Spread rate at complete hide | 7.85 $m^2/l$ | 7.97 $m^2/l$ | Equation 13.21 |

$$\text{Spread Rate (at complete hide)} = \text{Application Rate (as drawndown)} \times \left(\frac{\text{SX (as drawndown)}}{\text{SX (at complete hide)}}\right) \tag{13.21}$$

Similarly, we can calculate the film thickness at complete hiding as

$$\text{X (at complete hide)} = \text{X (as drawndown)} \times \left(\frac{\text{SX (at complete hide)}}{\text{SX (as drawndown)}}\right) \tag{13.22}$$

Note that there is an inverse relationship between film thickness and spread rate—as film thickness increases, spread rate decreases by the same factor.

We can solve the equations in this section for the paint described in the previous section and compare the calculated values of SX, $R_\infty$, and spread rate at complete hide to those read from the Judd Graph. This comparison is made in Table 13.2.

The spread rate at complete hide estimated from the Judd Graph is within 1.5% of that calculated using the Kubelka–Munk equations. This level of agreement is similar to the experimental error expected for the spread rate procedure [3, 4], confirming the validity of the Judd Graph.

## Spread Rate at Another Value of $R_\infty$

It is often the case that we wish to evaluate the scattering abilities of a group of paints that have different $R_\infty$ values. Directly comparing these paints is problematic because their appearances will be different at complete hide (some paints will be darker than others). We could correct for differences in paint brightness by toning all paints to a common $R_\infty$, but this would be painstaking to do in practice. However, we can do this mathematically by using the Kubelka–Munk equations to determine the spread rate of the paints when toned to a common $R_\infty$ value.

This process is computationally straightforward and is based on the strategy used to determine the spread rate at complete hide (described above). We will begin by using Eq. 13.9. In the previous section, we solved this equation using *a* and *b* values from the original drawdown. We cannot do that here because our hypothetical toned paints have different $R_\infty$ values than their untoned counterparts, so the values of *a* and *b* will be different for the toned and untoned paints (Eqs. 13.3–13.16). Instead, we will calculate the *a* value of the toned paint using Eq. 13.13, and then solve Eq. 13.20 (again with $R_g = 0.80$) for the value of R of the toned paint at complete hide. We can then solve for spread rate at complete hide using exactly the same procedure as described above.

## $R_\infty$ Values Greater Than 1.0

Consider a paint drawdown with a measured R value of 0.944 and a measured $R_o$ value of 0.85, giving a $C_r$ value of 0.90. The location of this paint on the Judd graph is shown as a green point in Fig. 13.7. This data point is noteworthy as it lies above the line for $R_\infty = 1.0$. Such a result is only possible if the light absorption coefficient, K, is less than zero. This, in turn, is only possible if the film created light—that is, rather than absorbing light, the film emits it. This can occur with the incorporation of a fluorescing agent, but such a situation is extremely rare in practice.

Although it is theoretically impossible for a drawdown to have an $R_\infty$ value greater than 1.0, such a result is occasionally seen in practice for very bright white paints. This situation can arise for a number of reasons that can be classified into two groups. The first is an experimental error in measuring the reflectance values. For example, the light intensity-measuring equipment could be poorly calibrated. Even a small departure from accurate calibration could lead to an $R_\infty$ value greater than 1.0 for paints that have very little light absorption (again, for very bright white paints). Another source of experimental error is not correcting for $R_g$ values that deviate from

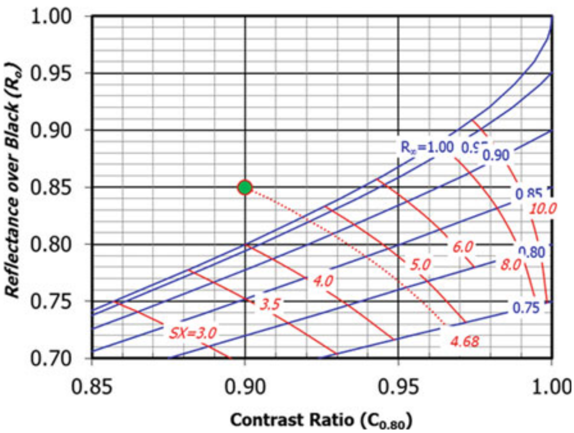



**Fig. 13.7** A data point with an $R_\infty$ value greater than 1

0.80. This source of error can be eliminated by measuring this value prior to use, as described above.

The second potential group of causes for an $R_\infty$ value being greater than 1.0 is a violation of one or more of the assumptions made in the Kubelka–Munk model. As noted above, the model does not take into account the reflection of light at the air/film and film/substrate interfaces. This can be problematic when comparing films with widely different gloss values or indices of refraction. In addition, the model assumes that the distributions of light scattering and light-absorbing particles are even throughout the film, which may not be true in flocculated systems. Finally, the model is based on the assumption that the light striking the film and within it is diffuse—that is, moving in all directions equally. Even in a perfectly dispersed paint, this assumption may be incorrect for the topmost layers of the film, where there may not have been enough scattering events to randomize the direction of the light entering the film from above. This complication would be most problematic for thin films.

Because $R_\infty$ values greater than 1.0 are seen on occasion, it is worthwhile to develop a strategy for dealing with this situation.

Before doing so, it is useful to discuss the implications of an $R_\infty$ value greater than 1.0. As noted above, the K value for the film becomes negative. In addition, we cannot calculate $R_\infty$ using Eq. 13.11, as the term within the radical (the radicand) is negative. When solving for $a$ using Eq. 13.7, we arrive at a value less than 1.0. This prevents us from solving for $b$ using Eq. 13.8, since the radicand in this equation will also be negative.

For paints that have calculated $R_\infty$ values greater than one, we can estimate SX by extrapolating the lines of constant SX in the Judd Graph to the region above $R_\infty = 1.0$. This can easily be done visually, particularly if the departure from the $R_\infty = 1.0$ curve is slight. However, calculating SX values in the $R_\infty = 1.0$ curve is more problematic, as we cannot use Eq. 13.11 due to the fact that $b$ is undefined.

This computational issue is resolved by turning to the derivation of Eq. 13.9. While this derivation is beyond the scope of this book, we note that one aspect of it involves the solution of a quadratic equation. As was the case in the section on spread rate at complete hide, there are two roots to such an equation. One root gives an $a$ value greater than one, leading to Eq. 13.9. The other root leads to an $a$ value less than one. It is this equation that will allow us to extend the lines of constant SX to the region of the Judd graph above $R_\infty = 1.0$. Solving for SX in the case of $a$ being less than one gives

$$\mathrm{SX} = \frac{1}{b}\mathrm{Arctg}\left[\frac{1 - a\mathrm{R_o}}{b\mathrm{R_o}}\right] \tag{13.23}$$

where Arctg is the arc-cotangent function ($\cot^{-1}$).

In Eq. 13.23, $a$ is calculated by Eq. 13.7, as before, and $b$ is calculated as

$$b = \sqrt{1 - a^2} \tag{13.24}$$

Equations 13.23 and 13.24 may seem familiar—as they should. We can see that they are very close to Eqs. 13.9 and 13.8, respectively, except the normal arc-cotangent function is used in Eq. 13.23 (rather than the hyperbolic arc-cotangent in Eq. 13.9), and the radicand in Eq. 13.24 is the negative counterpart of that in Eq. 13.8.

Equation 13.23 can be solved for the data point in Fig. 13.7, and its solution is depicted as the red dashed SX curve in this figure. Note that two equations are used to generate this SX curve—the region below the $R_\infty = 1.0$ curve is calculated using Eq. 13.9 while the region above the $R_\infty = 1.0$ line is calculated using Eq. 13.23. Based on these equations, we calculate the SX value of this paint to be 4.68.

The SX value of any drawdown with $R_\infty > 1.0$ can be calculated using Eqs. 13.26 and 13.27. However, solving for spread rate at complete hide ($C_r = 0.98$) when $R_\infty > 1.0$ is not always possible. For points that are far above the $R_\infty = 1.0$ curve, the radicand in Eq. 13.20 becomes negative, and R becomes undefined. We can therefore solve Eq. 13.20 only when the following condition is satisfied:

$$(C_r - 2aC_rR_g - 1)^2 \geq 4C_rR_g^2 \tag{13.25}$$

As noted above, when $R_\infty > 1.0$, the $a$ value is less than one. As we move to greater distances from the $R_\infty = 1.0$ curve, the $a$ value becomes progressively lower and eventually becomes so low that the radicand in Eq. 13.20 becomes negative (i.e., the condition described by Eq. 13.25 is no longer satisfied). This transition occurs when

$$a = \frac{2\left(\sqrt{C_rR_g^2}\right) - 1 + C_r}{2C_rR_g} \tag{13.26}$$

For an $R_g$ value of 0.80 and a contrast ratio of 0.98 (i. e., at full hide on a standard black and white card), $a$ cannot be below 0.9973974 if we are to solve for spread rate. It is the authors' experience that this situation is rarely encountered in practice. Should $a$ drop below this value, it is probably because the film deviates greatly from the Kubelka–Munk assumptions, in which case the analysis is likely to be invalid anyway.

## Examples and Commentary

By way of example, we will use the equations defined above to compare the spread rates of four hypothetical paints. Reflectivity information for these paints, and the optical properties derived from them, are given in Table 13.3. The location of these paints on the Judd Graph is given in Fig. 13.8 (note that, strictly speaking, the drawdowns of Paints C and D cannot be placed on this graph since their $R_g$ values are not 0.80. That said, the deviation of $R_g$ from 0.80 is slight enough to allow us to place these paints in Fig. 13.8).

**Table 13.3** Optical properties for four paints

| | Row | Property | Units | Paint | | | | Data source |
|---|---|---|---|---|---|---|---|---|
| | | | | A | B | C | D | |
| Paint and drawdown parameters | 1 | Paint Density | g/l | 1378 | 1378 | 1161 | 1161 | Measured |
| | 3 | Weight | grams | 3.76 | 3.76 | 3.01 | 3.01 | Measured |
| | 4 | Area | $cm^2$ | 350.0 | 350.0 | 350.0 | 350.0 | Measured |
| | 5 | $R_g$ | Unitless | 0.80 | 0.80 | 0.82 | 0.82 | Measured |
| | 6 | $R_o$ | Unitless | 0.83 | 0.85 | 0.81 | 0.82 | Measured |
| | 7 | R | Unitless | 0.87 | 0.89 | 0.90 | 0.93 | Measured |
| As drawn down | 8 | Contrast Ratio | Unitless | 0.954 | 0.950 | 0.900 | 0.882 | $= R_o/R$ |
| | 9 | SX | Unitless | 5.892 | 6.154 | 4.231 | 4.067 | Equation 13.9 |
| | 10 | KX | Unitless | 0.043 | 0.017 | −0.002 | −0.029 | Equation 13.10 |
| | 11 | *A* | Unitless | 1.0073 | 1.0028 | 0.9995 | 0.9930 | Equation 13.7 |
| | 12 | *B* | Unitless | 0.1210 | 0.0744 | 0.0305 | 0.1185 | Equation 13.8 or 13.24 |
| | 13 | $R_\infty$ | Unitless | 0.886 | 0.928 | XXX[13.1] | XXX[13.1] | Equation 13.11 |
| | 14 | X | microns | 78.0 | 78.0 | 74.2 | 74.2 | Equation 13.4 |
| | 15 | S | $microns^{-1}$ | 0.0755 | 0.0789 | 0.0570 | 0.0548 | = SX/X |
| | 16 | Application Rate | $m^2/l$ | 12.84 | 12.84 | 13.50 | 13.50 | Equation 13.5 |
| At complete hide (CR = 0.98) | 17 | Contrast Ratio | Unitless | 0.980 | 0.980 | 0.980 | 0.980 | Assumed |
| | 18 | $R_g$ | Unitless | 0.800 | 0.800 | 0.800 | 0.800 | Assumed |
| | 19 | $R_o$ | Unitless | 0.861 | 0.893 | 0.928 | XXX[13.1] | $= R \cdot CR$ |
| | 20 | R | Unitless | 0.878 | 0.911 | 0.947 | XXX[13.1] | Equation 13.20 |
| | 21 | SX | Unitless | 8.708 | 10.095 | 12.152 | XXX[13.1] | Equation 13.9 |
| | 22 | KX | Unitless | 0.063 | 0.028 | −0.006 | XXX[13.1] | Equation 13.10 |
| | 23 | *A* | Unitless | 1.0073 | 1.0028 | 0.9995 | 0.9930 | Equation 13.7 |
| | 24 | *b* | Unitless | 0.1210 | 0.0744 | 0.0305 | 0.1185 | Equation 13.8 or 13.24 |
| | 25 | X (thickness) | microns | 115.3 | 128.0 | 212.9 | XXX[13.1] | Equation 13.22 |
| | 26 | Spread Rate | $m^2/l$ | 8.69 | 7.83 | 4.69 | XXX[13.1] | Equation 13.21 |
| Hiding at new $R_\infty$ | 27 | Target $R_\infty$ | Unitless | 0.899 | 0.899 | 0.899 | 0.899 | Assumed |
| | 28 | Contrast Ratio | Unitless | 0.980 | 0.980 | 0.980 | 0.980 | Assumed |
| | 29 | $R_g$ | Unitless | 0.800 | 0.800 | 0.800 | 0.800 | Assumed |

(continued)

**Table 13.3** (continued)

| | Row | Property | Units | Paint | | | | Data source |
|---|---|---|---|---|---|---|---|---|
| | | | | A | B | C | D | |
| | 30 | $R_o$ | Unitless | 0.871 | 0.871 | 0.871 | 0.871 | = R•CR |
| | 31 | R | Unitless | 0.889 | 0.889 | 0.889 | 0.889 | Equation 13.20 |
| | 32 | SX | Unitless | 9.110 | 9.110 | 9.110 | 9.110 | Equation 13.9 |
| | 33 | KX | Unitless | 0.052 | 0.052 | 0.052 | 0.052 | Equation 13.10 |
| | 34 | *a* | Unitless | 1.0057 | 1.0057 | 1.0057 | 1.0057 | Equation 13.7 |
| | 35 | *b* | Unitless | 0.1067 | 0.1067 | 0.1067 | 0.1067 | Equation 13.8 or 13.24 |
| | 36 | X (thickness) | microns | 120.6 | 115.3 | 159.5 | 165.9 | Equation 13.22 |
| | 37 | Spread Rate | $m^2/l$ | 8.30 | 8.66 | 6.26 | 6.04 | = Row 26 x (Row 25/Row 36) |

[13.1] Incalculable

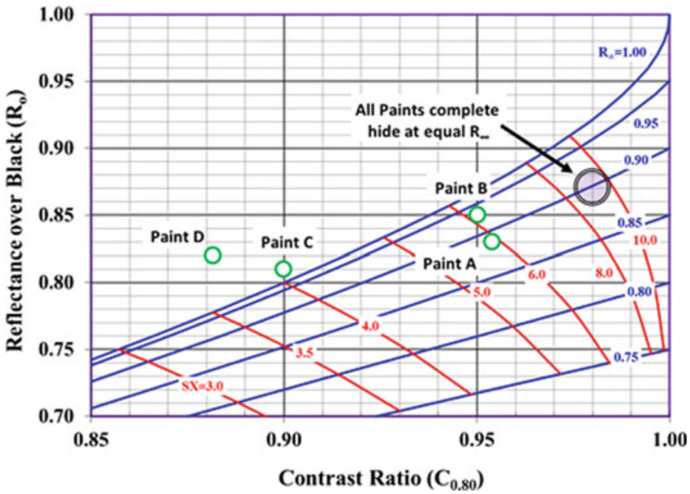



**Fig. 13.8** Judd Graph for the four paints described in the table

As can be seen in Fig. 13.8 and Row 13 in Table 13.3, and confirmed by Eq. 13.11, the $R_\infty$ values for Paints A and B are less than 1.0 while those for Paints C and D are greater than 1.0. Paint C falls close enough to the $R_\infty = 1.0$ curve that we can calculate its spread rate at complete hide, while the location of Paint D on the Judd Graph is far enough from the $R_\infty = 1.0$ curve that we cannot do this (Row 26).

The spread rates of Paints A and B at full hide (Row 26 in Table 13.3) show that, despite the fact that Paint B has greater scattering (Row 15), Paint A has a greater spread rate. This is because the $R_\infty$ values of the two paints are different (Row 13):

Paint A is darker (lower $R_\infty$) and its greater opacity is due to it having more light absorption than Paint B (Row 10).

Note that all paints, when adjusted to a common $R_\infty$ value of 0.90 and calculated at full hide (contrast ratio of 0.98), fall at the same location in the Judd Graph (large circle in Fig. 13.8). This means that the appearance (brightness) of these drawdowns would be identical to one another. As shown in Row 32, and by virtue of the fact that these drawdowns fall on the same point on the Judd Graph, under these conditions, the SX values of all the paints are also identical, as are their $R_\infty$ values (Row 27), *a* values (Row 34), and *b* values (Row 35) values. Although the SX values are identical, the S values are different. This results in the film thickness for complete hide being different (Row 36), leading to the different spread rates at equal brightness (Row 37).

## Applied Hide

In the previous section, we saw that the Kubelka–Munk equations link the reflectances of a paint film over both black and white backgrounds, the film thickness, and the absorption and scattering strengths of the paint (K and S). We used these equations to determine what we will call here the "intrinsic" hiding power of a paint, as expressed by the spread rate of the paint at the full hide. An important aspect of this analysis is that the measurements are on films that are uniformly applied by a blade or drawdown applicator. Film thickness uniformity is necessary if we are to have a single value for X with which to work.

In real-world applications, particularly those for which the paint is applied with a brush or roller, film thickness typically varies across the substrate in a series of peaks and valleys. This is seen as brush marks for paints applied by brush and stipple (also known as texture or roller marks) for paints applied by roller. Here, the meaning of film thickness and complete hide becomes uncertain—do we define spread rate based on the average film thickness needed for complete hide (i.e., measured as described in the previous section), or when the thinnest portions of the film are thick enough to obscure the substrate completely, or at some point in between? Do we report different spread rates for different types of applicators—brush versus roller, short versus long nap lengths on the roller, etc.? As we discuss this complication, we will refer to the perceived opacity of a paint film as applied by the intended applicator as being the "applied hide" of that film [8].

Intuitively we would expect that, at equal application rates, the uniformity of the film thickness would affect its perceived opacity, since a non-uniform application would result in some areas of the film being thicker than needed for complete hide and other areas being thinner than needed. The excess paint in the thick areas does not alter the appearance of those areas—as discussed when we defined $X_\infty$, all paint films above the thickness necessary for complete hide will appear the same. However, the deficit of paint in the thin areas leads to partial transparency of the film, with the substrate surface being detectible in these areas. Because of this, we expect the perceived opacity (and spread rate) from a given volume of paint to be greatest for an even film applied by a blade applicator and lower for an uneven film applied by a brush or roller.

## *Traditional Methods to Assess the Applied Hiding of an Architectural Coating*

The applied hiding power of an architectural coating can be assessed as described in ASTM D5150. Here, the paint is applied by a roller or a brush ontp a panel with six stripes going from light gray to black (see Fig. 13.9 for a white paint). The hiding power of the applied coatings is rated as the number of the darkest stripe that is completely (or almost completely) obscured, at a specified thickness or spread rate.

Although this rating appears straightforward, there are several limitations associated with the method:

(1) When one applies a paint with a roller or a brush, it is very difficult to accurately control the applied thickness, hence the hiding power might differ from one area to the other.
(2) The assessment of which strips are completely covered is determined by eye and so is very subjective.
(3) Comparing paints with different flow characteristics (different formation of peaks and valleys) is very difficult and also subjective.

In practice, paint producers have several variants of this method. One that is seen on a regular basis is that a trained applicator applies the paint on a (partially) black substrate. After drying, panels are rated versus a set of numbered reference panels

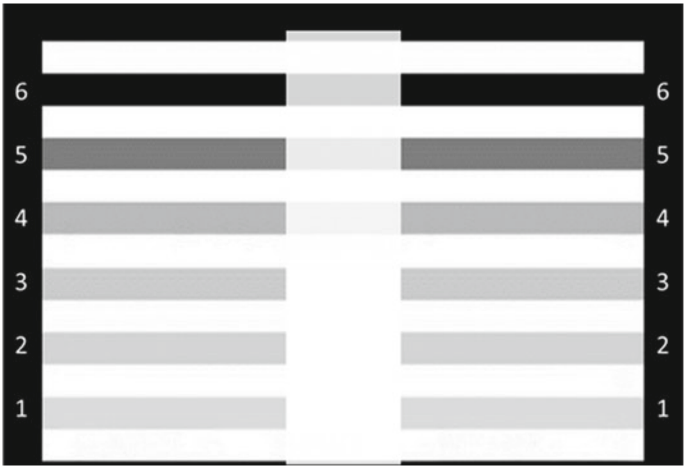



**Fig. 13.9** Application panel used to determine the applied hiding power as described in ASTM 5150. A white paint has been applied to this panel. The rating for this paint is 3

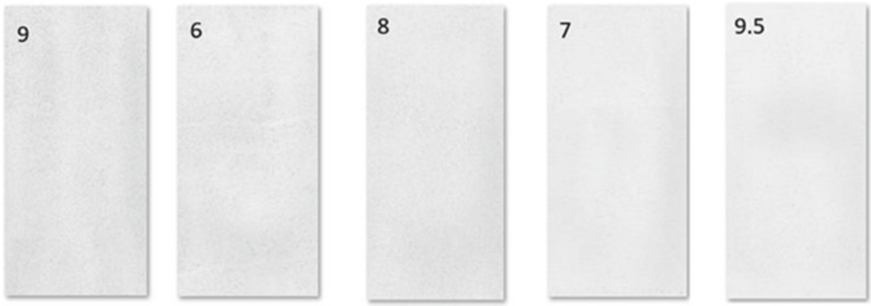



**Fig. 13.10** Applied hiding panels of the same paint, applied by five different trained painters. The numbers represent the rating given by each painter of their own panel, and the order of the panels goes from poorest hiding (left) to highest hiding (right)

that span the range from very poor hiding to very good hiding. If the result is very close to the reference panel number 8, the test panel is given a rating of 8. However, there is some ambiguity and there are inconsistencies in how to rate a test panel that lies between two reference panels—this is, these variants of the ASTM method do not overcome the limitations of the original method.

This issue is illustrated by an experiment in which five trained painters were asked to apply the same paint to a gray substrate and to independently rate their results against the same set of reference panels. The panels, as well as the ratings, are shown in Fig. 13.10. If the method was very reproducible, we would expect the same result (both in terms of visual appearance and rating) for the five painters. Clearly, this is not the case.

Two observations can be made from this small series of panels. First, although the paint, rollers, substrates, drying conditions, etc., were all identical, it is clear that there is a high degree of visual variability between the panels. The second observation is that there is not only variation in the visual appearance of the panels, but also in the perceived rating by the painters. Importantly, there is a complete lack of correlation between the visual appearance of the panel (demonstrated by the panel order from left to right in Fig. 13.10) and its assigned rating.

It is clear from even this limited assessment that the rated panel method suffers a high level of variability. To overcome this deficiency, a new test, based on the objective measurement of the panel appearance using an image scanner and algorithmic-based analysis of the measured data, was developed [8]. This test is described in the following section.

## *An Alternative Method for Applied Hide*

Any alternative method for applied hide analysis cannot be based on appearance as determined by the eye and must instead be read by an instrument. A typical colorimeter cannot be used to make this assessment as it measures only a limited area of the sample (the aperture of the colorimeter is typically a few $cm^2$), and our interest is in the appearance uniformity across the entire painted surface. In addition, these instruments can only give an average value of opacity over this area while we are interested instead in the variability of opacity. This variability, which is due to the peaks and valleys in the paint film, is over a much smaller scale than the colorimeter can resolve.

To overcome the low resolution and the limited investigated surface area when using a colorimeter, a commercial, high-resolution flat-bed scanner (A3 format) can be used to measure the color (reflectance) of every pixel of the painted panel. Figure 13.11 shows schematically the technique and example results.

The pixels with reflectance values equal to $R_\infty$ are fully hiding and are indicated in bright green in Fig. 13.11. As the scanner is more sensitive than the average human eye, the pixels with reflectance values close, but not equal, to $R_\infty$ will also be perceived as fully hiding. These pixels are indicated in pale green in this figure. However, as the reflectance values deviate more significantly from $R_\infty$, the pixels will be visually perceived as being different than $R_\infty$. These pixels can be grouped into three additional classes: pixels with moderate hiding power (orange in Fig. 13.11), low hiding power (red), and very low hiding power (black), and the number (or percentage) of the pixels in each class can be calculated. We now can define the applied hiding as the percentage of pixels that are at least moderately hiding (pixels in yellow, light green, and dark green). In Fig. 13.11, this represents about 80% of the covered area.

The Kubelka–Munk equations for each pixel can be solved by knowing the reflectance value of the pixel and the Kubelka–Munk parameters (K and S) from

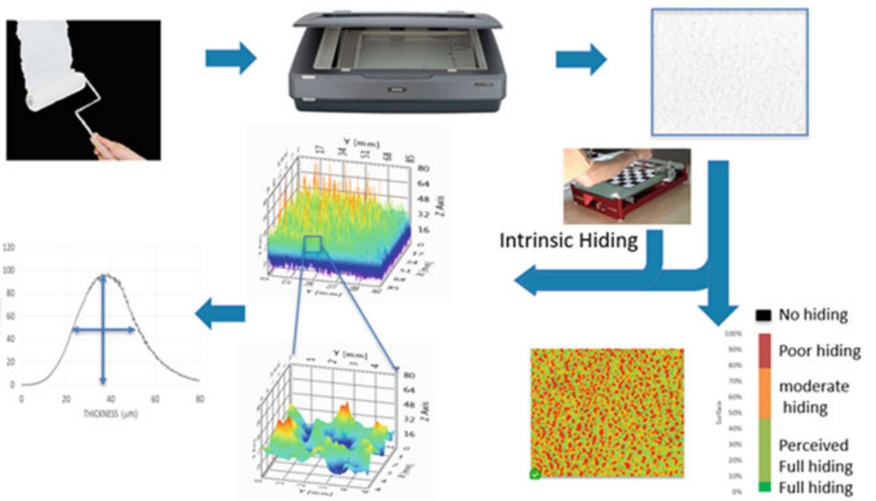



**Fig. 13.11** Schematic representation of the scanning method to quantify the applied hiding and to generate a 3D image of the scanned panel

the intrinsic hiding power test (discussed earlier in this chapter). From this, we can determine the film thickness, Xi, for every pixel. Plotting this thickness results in a three-dimensional image from which the distribution of thicknesses across the scanned surface can be calculated. Note that in this procedure, the Kubelka–Munk equations are used in two different ways: First, to determine the intrinsic hiding power, K and S, starting from a measured film thickness and reflectance values from a uniform drawdown, and second, to calculate the thickness value Xi for each pixel in the roller or brush applied film using from the measured reflectances and the calculated K and S.

As a verification of this approach, a paint was applied with a drawdown bar with stepped clearances (Fig. 13.12). Figure 13.12a shows the drawdown card used in this test, and Fig. 13.12b shows the profilometer profiles of the paint over the black and

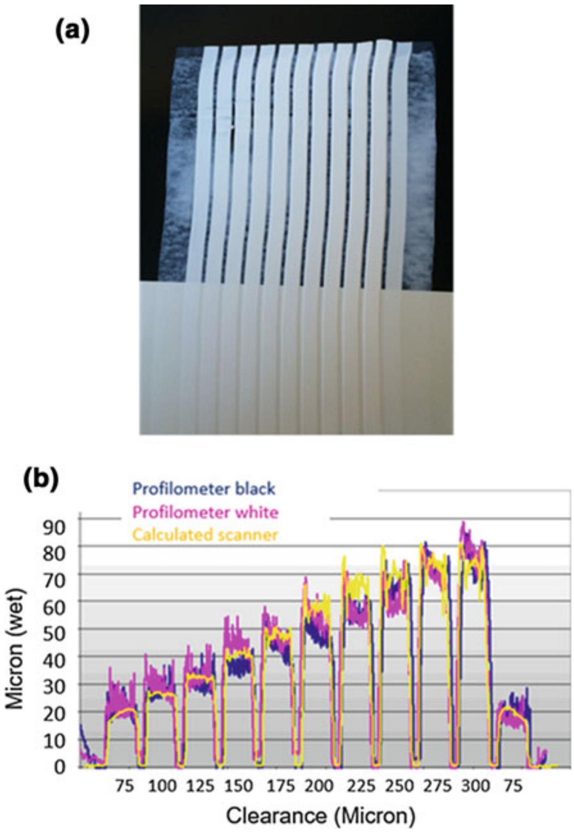



**Fig. 13.12** **a** Drawdown of an architectural coating with a drawdown bar with stepped clearances from 75 to 300 micron in steps of 25 micron. **b** Calculated wet film thickness values using the applied hide methodology and adjusted thicknesses as measured by profilometry

white portions of the card as well as the dry film thickness values calculated from the scan as described in Fig. 13.11.

As the thicknesses are all expressed as wet film thickness, a correction is applied taking into account the volume solids of the paint. As can be seen, there is excellent agreement between the thickness measured via a profilometer (after correction for the volume solids) and the thickness calculated via the scanner and the Kubelka–Munk equations. Note there is a significant discrepancy between the clearances X-axis values) and the actual wet film thicknesses (Y-axis values), as discussed in the section on contrast ratio limitations above, that is attributed to the rheology of the paint.

## *Applied Hide Example*

As an example of the effect of average film thickness on applied hide, a wall paint was loaded onto a roller and applied to a series of six black opacity charts without reloading between applications. Panels were weighed before and after application to determine the amount of applied paint. Knowing the density and the surface area of the panel, the average thickness of the paint can be calculated as indicated in Fig. 13.13.

Figure 13.13 shows that initially (left image in this figure) the paint hides the black substrate quite well. However, as the number of painted panels increases, less paint is transferred from the roller to the substrate. As a result, the thickness of the layer decreases, and the black surface becomes increasingly visible. The lower part of the figure is the translation of the visual image to the pseudo-color scale as defined in a previous paragraph and shown in Fig. 13.11.

The bar chart in Fig. 13.14a shows the percent of the surface area of each hiding classification for each panel shown in Fig. 13.13. The graph in Fig. 13.14b shows

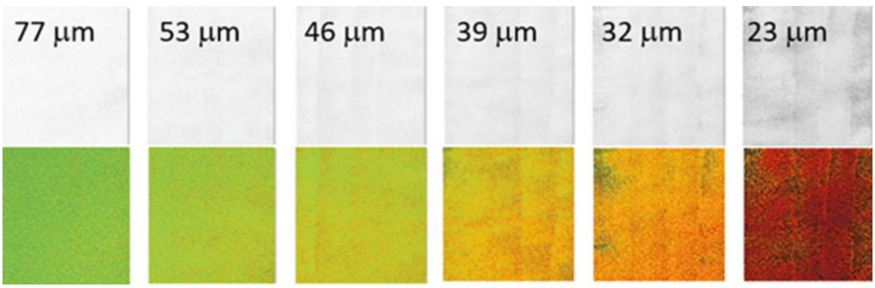



**Fig. 13.13** Application of a single roller load of a paint onto six black opacity charts. The leftmost image is the first application, and the rightmost image is the sixth. The numbers shown are the average wet film thicknesses of the coating. The upper part of each represents the visual images, and lower shows the translation of each image into pseudo-color scale (see Fig. 13.11)

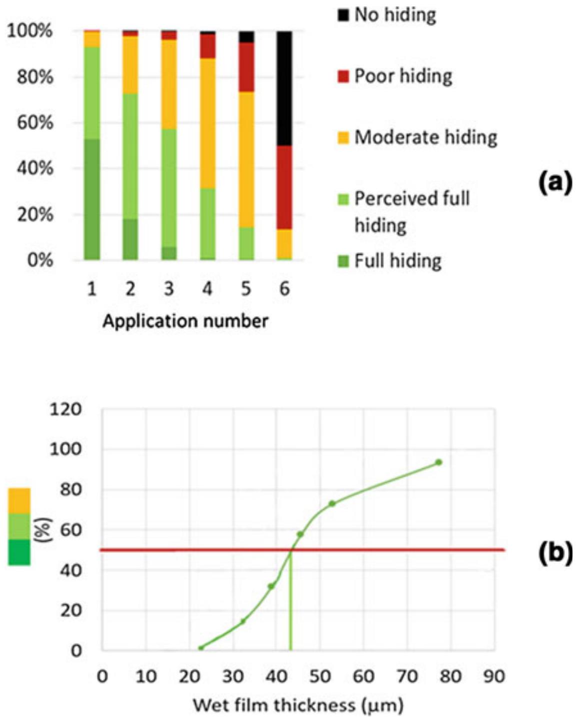



**Fig. 13.14** Image analysis results for multiple applications without reloading roller. **a** Bar chart showing the total surface of the different hiding classes. **b** Total percent of the surface area classified as moderate (yellow), perceived (light green), and full (dark green) hiding as a function of average wet film thickness for each drawdown

the total surface area covered at incomplete, perceived, and full hiding (defined in Fig. 13.11) with the average thickness of the applied paint.

Figure 14b shows that about 43 microns of wet film thickness are required to cover 50% of the surface area with at least moderate hide. We define this number as the applied hiding power. This number is characteristic of a paint and roller combination, and is independent on the amount of paint initially loaded onto the roller.

This is illustrated in a study in which two painters applied the same paint with the same type of roller. Each painter loaded the roller and made seven applications onto black opacity charts without reloading the roller. The resulting drawdowns are shown in Fig. 13.15. As can be seen visually, there are significant differences between the two drawdown series. Since the paint and roller are the same in each series, the only remaining variable is the painter. Apparently, these painters had different techniques and preferences for loading and applying paint by roller. This again illustrates the difficulty in reproducibly applying paint by roller, as was also shown in Fig. 13.10.

Although the paint series clearly differed in appearance, when the panels were scanned and the percent surface area with at least a moderate degree of hiding was plotted versus the wet film thickness (Fig. 13.16), the results for both painters fell on the same curve. In particular, the same wet film thickness—35 microns—was necessary to give 50% of the surface with at least a moderate hiding. This is not surprising since this coverage amount should be a property of the paint itself. This

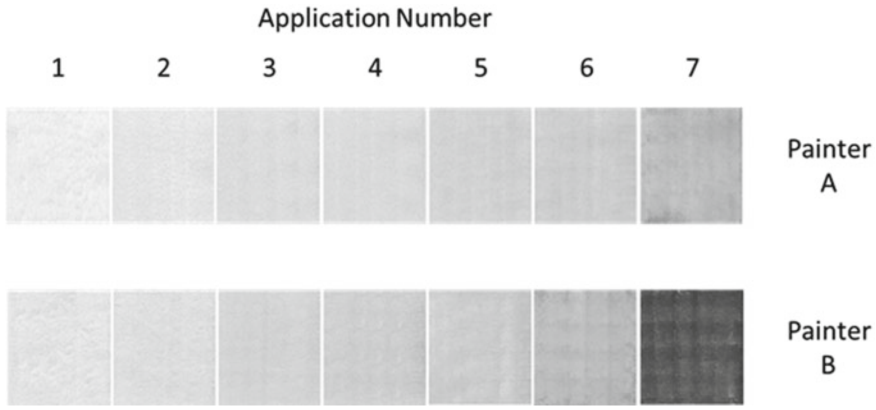
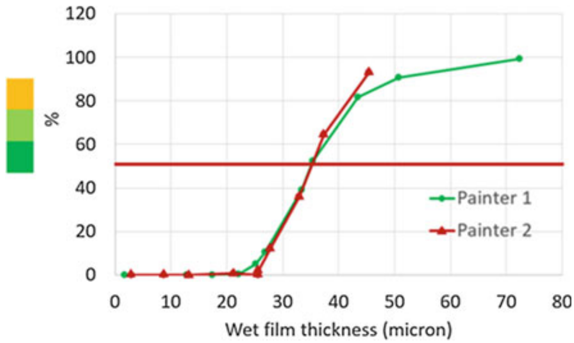



**Fig. 13.15** Multiple rollouts of the same white paint onto a black substrate using the same roller, as applied by two different professional painters

**Fig. 13.16** Percent surface area with moderate hiding power for both painters




illustrates the high degree of reproducibility for this method of determining applied hide.

### *Factors Affecting Applied Hide*

We expect applied hiding power to be controlled by several paint and film parameters. Obviously, it is dependent on the intrinsic hiding power of the paint. In addition, it depends on the degree to which the applied paint thickness is uneven. We will call this property the "structure" of the dry paint film, and we note that structure depends primarily on the rheology (flow kinetics) of the paint and the exact nature of the roller that is used to apply the paint. The effect of the latter is outside the scope of this book. The drying kinetics (the so-called open times) are also important because longer drying times provide more opportunity for the initially structured paint surface,

**Table 13.4** Overview of the properties that affect applied hiding power for four commercial paints

| Property | Paint A | Paint B | Paint C | Paint D |
|---|---|---|---|---|
| Intrinsic hiding ($m^2$/l) | 14.6 | 11.6 | 15.3 | 12.3 |
| Flow characteristic | Pseudo plastic | Newtonian | Highly pseudoplastic | Pseudo Plastic |
| Wet film thickness for 50% of the surface to have moderate hiding power | 31 microns | 40 microns | 34 microns | 44 microns |

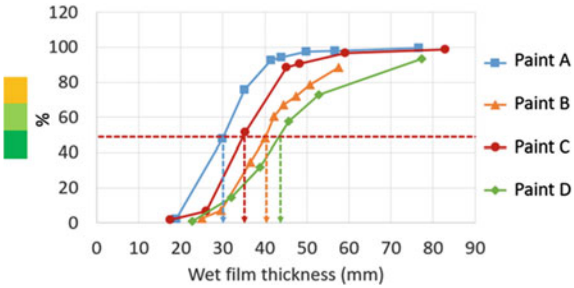



**Fig. 13.17** Percent surface area with moderate hiding power as a function of the wet film thickness for four commercial paints

as formed by the roller, to flow and become even. Although drying kinetics play an important role in the applied hide, this factor is also beyond the scope of this book and will not be discussed here.

The importance of paint flow to applied hide was investigated using four commercial paints with different flow characteristics and intrinsic hiding powers (Table 13.4). These four paints were applied and analyzed in a roll-out experiment as described in the previous paragraph. The applied hide results for these paints are shown in Fig. 13.17.

Figure 13.17 shows that the required wet film thickness to reach 50% surface area of at least moderate coverage for these four paints ranges between 31 and 44 microns.[5] Despite the high intrinsic hiding power of Paint C, more of it is required to reach moderate coverage for 50% of the surface area than of Paint A, which has a lower intrinsic hiding power. This is due to the very pseudoplastic behavior of Paint C, which results in it having a very structured surface and larger variability in film thickness. This, in turn, results in a relatively large area having poor coverage.

Paint B has the lowest intrinsic hiding but flows relatively well, resulting in an even surface and a lower required wet film thickness than expected based on the other paints. Paint A combines high intrinsic hiding with relatively good flow properties resulting in the highest applied hiding power. Paint D, by contrast, has lower intrinsic hiding and worse flow than Paint A, giving it the worst applied hiding power of the series.

[5] Note that these paints do not necessarily bracket the range generally seen for commercial paints and that these values may vary largely for other paints.

## Paint Rheology

As suggested in the paragraph above, we expect the structure to be related to the rheology of the liquid paint. If the paint flows freely under zero shear conditions (e.g., after application of the paint), then surface tension should eliminate irregularities in wet film thickness, thereby minimizing structure and improving the applied hide. However, the free flow of paint after an application is generally undesirable as it results in sagging and running of the wet paint. This severely limits the amount of paint that can be applied in a single application to vertical surfaces. The rheology required for acceptable flow and leveling creates a trade-off between these properties and applied hide.

Depending on the nature of the thickener and the interactions between the different ingredients, the rheology profile of a paint will be pseudoplastic, Newtonian, or somewhere between (Fig. 13.18). The viscosity of a true Newtonian liquid is independent of the shear rate (green line in Fig. 13.18) while for a pseudoplastic paint the viscosity will decrease significantly with increasing shear rate (shear thinning) following the solid red line in Fig. 13.18. When the shear is removed, the viscosity will build up again, following the dotted line.

The rheology profile of a paint has great significance in many of its application properties. During the painting process, the shear rate increases to between 1000 and 10,000 $s^{-1}$. A low viscosity in this domain provides easier application, but more difficultly in achieving a sufficiently thick layer of paint for complete hide. A low viscosity at low shear rates (0.1 $s^{-1}$) can cause sagging if the paint is applied too thickly while a high viscosity at low shear rates can result in poor leveling of the wet paint. In this context, the leveling can be seen as the peaks filling the valleys. High viscosity at very low shear rates (0.001 $s^{-1}$) can prevent the settling of the paint on storage. A paint formulator must invest much time and effort to find the right balance between these different rheological parameters.

To illustrate the effect of rheology on applied hide, four paints were made with exactly the same amounts of $TiO_2$, extenders, resin, etc., but differing in the rheology package. These were applied to panels, images of which are shown in Fig. 13.19.

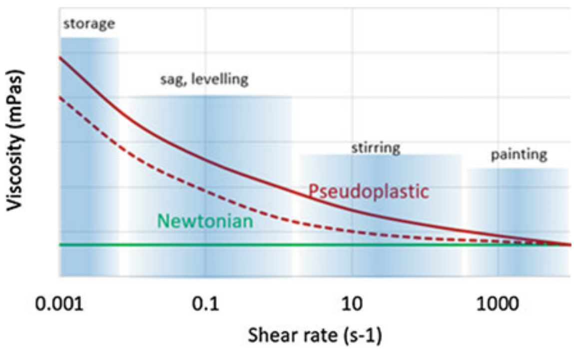



**Fig. 13.18** Schematic representation of the two archetypical rheology profiles in coatings

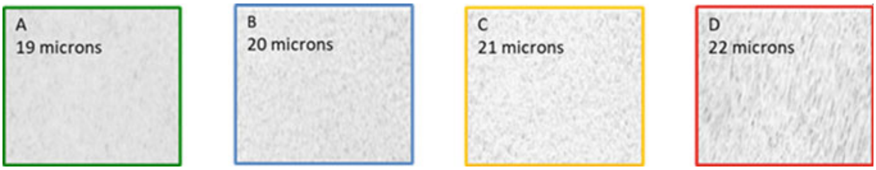



**Fig. 13.19** Application of four paints with differing in rheology only. The numbers indicate the average wet film thickness in microns

Paint A contains a Newtonian thickener, while Paint D contains a very pseudoplastic thickener. The two paints in the middle contain thickeners that give intermediate behaviors. All paints were brought to similar high shear ("ICI") viscosities and applied with the same roller type at roughly the same average wet film thickness (ranging between 19 and 22 microns).

Paint D, with pseudoplastic rheology, shows a high degree of brightness variability, with both very white areas and very dark areas. As the rheology becomes more Newtonian (moving from right to left in Fig. 13.19), the variability in brightness decreases, and the images become more uniformly gray.

Three-dimensional reconstructions of film thickness, using the same format as Fig. 13.11, are shown in Fig. 13.20. While the average wet film thicknesses of the paints are all close to 20 microns, the peaks and valleys are much more pronounced in the pseudoplastic paint (Paint D) compared to the Newtonian paint (Paint A). Paints B and C show intermediate levels of height variability. This observation is in line with the proposition that the viscosity of a pseudoplastic paint drops during the roller application (high shear) but builds after application (low shear), preventing the paint from leveling during drying. The viscosity of the Newtonian paint, on the other hand, remains relatively low throughout the application and drying process, allowing paint to flow from patches of high thickness to those of low thickness. This results in a more even thickness and so a more even opacity across the paint.

Figure 13.21 quantifies the degree of image uniformity in Fig. 13.19 using histograms of the wet film thickness values for each pixel in these images. The widths of these histograms correspond directly to image uniformity. As the rheological behaviors of the paints become more Newtonian (i.e., in going from Paint D to Paint A), the curves become sharper and the appearance of the paint more uniform.

The Newtonian paint (Paint A) has very few pixels with very thin (<10 micron) or very thick (>40 micron) calculated thicknesses. By contrast, the pseudoplastic paint (Paint D) shows a significant number of pixels at these two thickness extremes. It is worth noting that pixels at either end of the thickness extremes are undesirable. Obviously, those at the low end look dark, and so contribute directly to a non-uniform appearance and a low applied hide. This contributes to a pattern of strong contrasts in Paint D, which attracts the human eye and contributes strongly to the perception of incomplete covering. On the other hand, while excessively thick regions do not look different from other regions with acceptable hide, they represent a waste of paint.

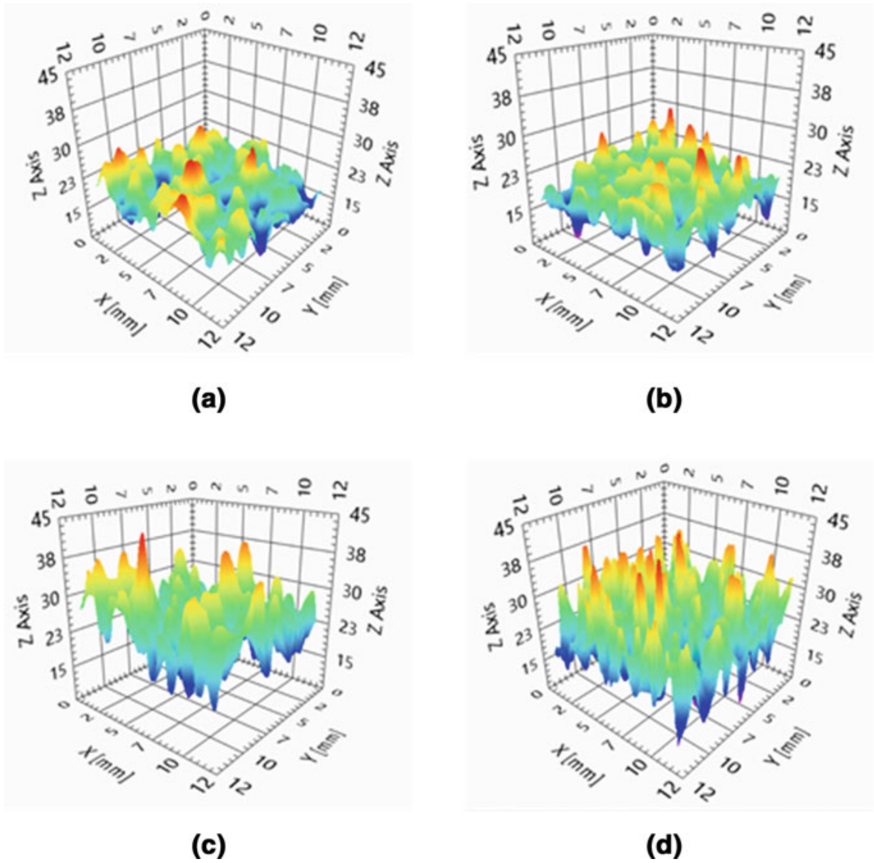



**Fig. 13.20** Three-dimensional representations of the four paints shown in Fig. 13.19. **a** Newtonian rheology. **b** and **c** intermediate rheology. **d** pseudoplastic rheology

These pixels would look the same if a portion of paint was removed from them and redistributed to areas of thin coverage.

The applied hide shown in Fig. 13.19 for Paint D is unacceptable for most paint applications. This deficiency can be overcome in one of three ways. First, we could apply a second coat of this paint. This would shift the histogram to higher thicknesses and so reduce the number of overly thin pixels.[6] While this results in acceptable applied hide, it increases both the cost of labor (to apply a second coat[7]) and the cost of coverage by the paint (to make a thicker coating).

[6] Due to the nature of counting statistics, we would expect this effect to be somewhat offset by an increase in curve width.

[7] This may not be strictly true, since paints are physically more difficult to apply at a higher build, and so this may slow the speed of the painter.

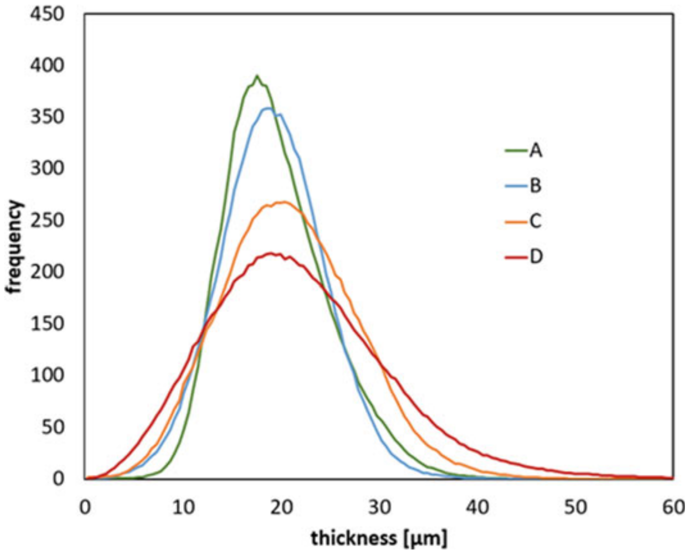



**Fig. 13.21** Histogram of the number of pixels at a certain wet film thickness for a paint with a Newtonian rheology package (A), a pseudoplastic rheology package (D), and two intermediate cases (B and C)

Alternatively, we can simply increase the film build—that is, increased the amount of wet paint applied to the substrate during a single application. While this can be done without increasing labor costs, it, too, suffers from an increased cost of raw materials, due to the increase in average film thickness.

Finally, the rheological behavior of this paint can be made more Newtonian, to sharpen the histogram curve without shifting its average. While this option maintains the original average film thickness while increasing opacity, it is less costly than the other alternatives. However, this leads to a greater sensitivity of the wet paint to sagging, which limits film build. If the film build is restricted due to sag, then it must be applied in two coats, increasing labor costs.

We see, then, that the formulator is challenged to find the best overall rheological behavior to minimize non-uniformity in film thickness while maximizing the amount of paint that can be applied in one application.

## Tinting Strength

In a completely opaque film, all light entering the film is either redirected back from it via light scattering before interacting with the substrate or is terminated within the film by light absorption. The brightness of the film is determined by, among other factors, the distance that the light travels within the film. This distance will be greater for films with weak light scattering than for films with strong light scattering, and greater for films with weak light absorption than for films with strong light absorption. Since high opacity is found when light scattering and light absorption are at their highest, we can use the distance traveled through the film as a proxy for opacity. Longer distances give lower opacity, since light penetrates more deeply into the film as the path length increases.

Opacity can therefore be measured as the distance that the light travels within a film. To directly measure this distance by tracing the paths of photons through the film is impossible. However, a quite viable alternative is available to us—light absorption. In Chap. 8, we discussed the Beer–Lambert law, which relates the amount of light absorbed by an object to three parameters—the absorption strength of a unit amount of light-absorbing material (colorant, for paints), the concentration of this light-absorbing material, and the distance the light travels. This law is summarized in Eq. 13.27:

$$A_\lambda = \varepsilon_\lambda bC \tag{13.27}$$

where $\varepsilon_\lambda$ is the absorption coefficient of the colorant, b is the path length through the object, and C is the concentration of the colorant.

The relationship given in Eq. 13.27 suggests that film reflectance (brightness) could be used as an indirect means of measuring the average distance that light travels through an opaque film. Because a tinted paint is required for this measurement, it is referred to as a tinting strength test. We could, in theory, use the reflectance measurement to calculate the actual distance that the light travels through the film. However, this is a laborious and unnecessary task. Instead, this test is almost always performed with a standard that has a defined tinting strength (typically an assigned value of 100) [9].

Both absorption strength and scattering strength determine light penetration distance, and so the tinting strength test can be used in two ways: either to compare the light scattering abilities of different $TiO_2$ samples or to compare the light absorption abilities of different color pigment samples. The critical difference between these two forms of testing is in how we attribute any differences in reflectance between a test paint and the control paint. If we are comparing the performance of $TiO_2$ pigments, say two batches of the same pigment, or samples from two suppliers, then any reflectance differences are assumed to arise from differences in scattering strength of the $TiO_2$. If we are comparing the performances of two color pigments, then we attribute any differences in reflectance to differences in the light absorption strength of the color pigment.

## *Tinting Strength of the White Pigment*

The two versions of testing are fairly straightforward to run, but with some subtle yet crucial differences in how the actual tinting strength values are calculated. To measure the tinting strength of the $TiO_2$, colored paints with the $TiO_2$ samples of interest (including a standard) are made with reflectivities around 0.40 to 0.50 (measured as Tristimulus Y). The colorant can either be one that is familiar to the experimenter or carbon black. The latter is specified for the ASTM method for this test [3]. The paints are then drawn down at a thickness great enough to ensure complete opacity, dried under controlled conditions, and the reflectance of the drawdowns measured. If a color pigment is used, we have a choice as to which reflectance values to use for this test, either the reflectance at the wavelength of maximum absorption strength of the color pigment, or the tristimulus Y value (total reflectance at all wavelengths). When a black pigment is used in the test, the tristimulus Y value is taken as the reflectance.

Since the films are drawn down at a great enough thickness to achieve complete opacity, the measured R values can be assumed to be the $R_\infty$ values for the paints. In this situation, we can apply the Kubelka–Munk theory to determine the balance between light absorption and light scattering (K/S) using Eq. 13.12.

The tinting strength of the standard paint is assigned a value of 100, and the tinting strength of an unknown is calculated as [10]

$$\mathrm{TS}_{\mathrm{Unknown}} = \frac{(K/S)_{\mathrm{Standard}}}{(K/S)_{\mathrm{Unknown}}} \times \mathrm{TS}_{\mathrm{Standard}} \tag{13.28}$$

where K/S values are calculated using Eq. 13.12 and the $\mathrm{TS}_{\mathrm{standard}}$ is normally assigned a value of 100. Assuming that the absorption strength K of the colorant is the same in all paints—that is, any differences in reflectivity are due to differences in $TiO_2$ scattering strength—Eq. 13.28 reduces to

$$\mathrm{TS}_{\mathrm{Unknown}} = \frac{1/S_{\mathrm{standard}}}{1/S_{\mathrm{Unknown}}} \times \mathrm{TS}_{\mathrm{Standard}}$$

$$\mathrm{TS}_{\mathrm{Unknown}} = 100 \times \frac{S_{\mathrm{Unknown}}}{S_{\mathrm{Standard}}} \tag{13.29}$$

A drawdown example showing under-dispersion of the $TiO_2$ pigment is shown in Fig. 13.22.


**Fig. 13.22** Tinting strength test for $TiO_2$. Difference in drawdown brightness is due to the degree of $TiO_2$ dispersion

## *Tinting Strength of the Color Pigment*

Alternatively, the tinting strength test can be used to compare the absorption strengths of two color pigment samples. Again, two paints are made. In this case, the same $TiO_2$ is used for both paints, with one paint containing the standard color pigment and the other the unknown color pigment. Dark paints are diluted with equal amounts of white paints to give a reflectance value in the range of 0.34 to 0.45. Drawdowns are again made at complete opacity, and the R, G, and B tristimulus values of the films are measured [12]. Of these three, the tristimulus value closest to the color of the paints is used to calculate the tinting strength of the unknown pigment as follows:

$$\mathrm{TS}_{\mathrm{Unknown}} = \frac{(K/S)_{\mathrm{Unknown}}}{(K/S)_{\mathrm{Standard}}} \times \mathrm{TS}_{\mathrm{Standard}} \tag{13.30}$$

Assuming that the scattering values of the paint are identical, this reduces to the counterpart of Eq. 13.29:

$$\mathrm{TS}_{\mathrm{Unknown}} = 100 \times \frac{K_{\mathrm{Standard}}}{K_{\mathrm{Unknown}}} \tag{13.31}$$

Note that Eqs. (13.28) and (13.30) are inverses of one another. In this way, a tinting strength value greater than 100 means that the optical property of interest (scattering or absorption) will exceed 100 if that property is greater in the unknown paint than in the standard. However, the meaning of a brighter test paint than control is dependent on the test type—this would indicate low tinting strength for a color pigment or high tinting strength for a $TiO_2$ pigment.

## *Color Development and Shear Strength Uniformity*

A test closely related to the tinting strength test is used to determine whether the degree of pigment dispersion in a paint is complete. Under-dispersion of either the white pigment or the color pigment will lead to the need for excessive levels of that pigment.

There can be different causes for under-dispersion. The two most common are incomplete dispersion during paint production and pigment flocculation during storage or drying. Both can apply to either the white pigment or the color pigment(s). Regardless of which type of pigment is under-dispersed, the degree of under-dispersion can be determined in the same way. The paint of interest is drawn down at complete hide and allowed to dry. Fresh paint is applied to a portion of the drawn-down film and subjected to a high level of shear. This shear should be sufficient to disperse any under-dispersed pigment. If under-dispersion is present in the paint, the appearance of the drawndown area and the highly sheared area will be different.

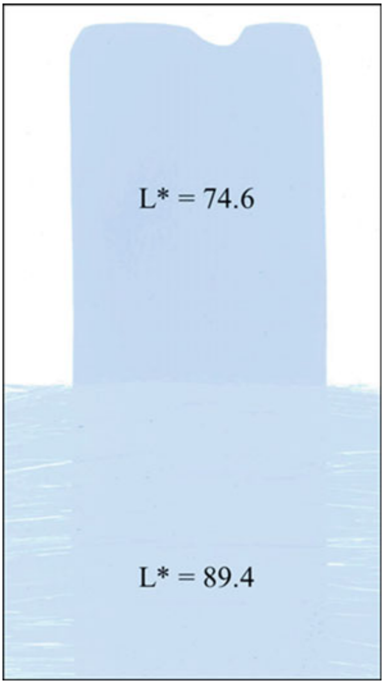
Historically, the additional shear was applied by rubbing the wet paint with a finger or thumb—the so-called "rub-out" test. However, the shear is not well controlled in this case, and there can be a great deal of variability in the degree to which the two portions of the drawdown film appear different, depending on the shear level. To overcome this variability, ASTM has developed a specific way of applying shear to the wet film using a brush [12]. In addition, in some procedures, the initial coat of paint is sheared after a set amount of drying, rather than allowing the first coat to dry completely and then applying a layer of fresh coat.[8]

Once the added paint has dried, the reflectance values of the two areas are compared. In some cases, appearance differences are easily seen visually. In other cases, the shift in color is too slight to be apparent. In any event, the reflectance measurements of the paint are measured and their difference, if any, is determined. This can be either as a $\Delta E$ value or as a difference in brightness (tristimulus Y).

The identity of the flocculated pigment is determined by whether the sheared area is brighter or darker than the unsheared (drawn down) area. If the $TiO_2$ is partially flocculated, the sheared area will be brighter than the drawndown area (that is, shearing improves light scattering). If the color pigment is partially flocculated, then the sheared area will be darker than the drawndown area. A shear strength

[8] Using two coats of paint is generally preferred for the following reason: The shear applied to the paint, especially if it has partly dried and is tacky, results in a non-uniform thickness. In thin areas, the background can be seen. In this case, it is better for that background to be the color of interest rather than white. In this way, if there is no dispersion after shear, the color of the sheared and unsheared portions of the drawdown will appear identical. If only one coat is applied and a portion sheared when the paint is tacky, then it will generally appear lighter than the unsheared portion for the reasons discussed in the section on applied hide.

**Fig. 13.23** Shear strength uniformity drawdown for the paint shown in Fig. 13.22. The top area is as drawn down; the lower area is after shearing with a brush




uniformity drawdown card for the under-dispersed $TiO_2$ paint in Fig. 13.22 is shown in Fig. 13.23.

## Undertone

Our analyses in this chapter have so far omitted any mention of wavelength when discussing light scattering. Obviously, the wavelength is very important for light absorption by a chromatic pigment, with the absorption strength of a color pigment being a strong function of wavelength. Less obviously, light scattering is also wavelength dependent. This was touched on in Chap. 3, where we discussed the importance of matching particle size to light wavelength in determining the scattering strength of a particle. There we focused on particle size, but light wavelength can have an even stronger effect on scattering strength. This is because the match between particle size and wavelength depends equally on both and because the refractive index of a particle is wavelength dependent (for example, the refractive index of rutile $TiO_2$ in the visible region of the light spectrum drops from 2.91 at 380 nm to 2.48 at 700 nm) [13]. The combined effects of this are shown in Fig. 13.24 [2].

The importance of this has two sources. The first is that the strength of light diffraction—the primary mechanism of light scattering by $TiO_2$ particles—depends

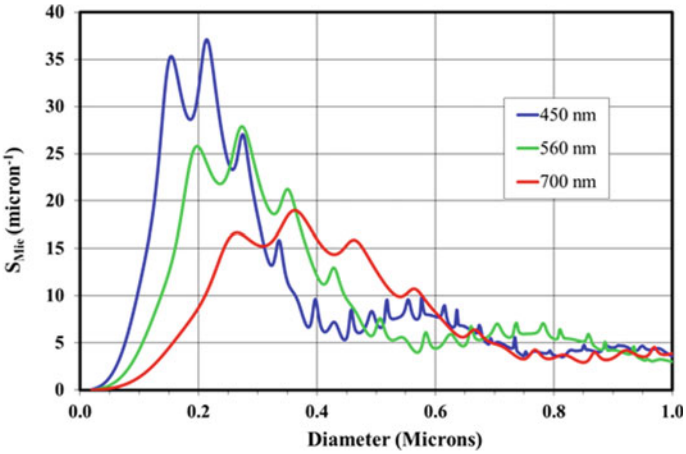



**Fig. 13.24** Calculated light scattering from a single $TiO_2$ particle as a function of light wavelength and particle size

on the ratio of wavelength and particle size, and so if we hold particle size constant, we would expect scattering strength to vary with wavelength. The second source is an indirect one: in addition to particle size, scattering strength depends on the difference in refractive indices of the scattering particle and the surrounding medium. The refractive index of $TiO_2$ varies with wavelength and is a maximum at the blue end of the visible spectrum and decreases significantly as wavelength increases to the red end. The refractive index of resin varies little over this wavelength range, so the difference in refractive indices between the particle and its surroundings decreases as the wavelength increases.

The overall effects of these two components of scattering strength are that the path length of blue light through a paint film is shorter than that of red light, at least within the range of $TiO_2$ particle sizes that maximize visible light scattering. This difference in path length is different for different $TiO_2$ particle sizes. This difference is typically characterized as the ratio of blue scattering strength to red scattering strength, and this ratio can be used to characterize the average particle size of the $TiO_2$ particles. This ratio, which is referred to as the undertone of the $TiO_2$, makes a contribution to the color of a chromatic paint, and differences in particle size between one pigment sample and another can cause a subtle, but observable, shift in paint color. In particular, smaller particles have a bluish undertone, while larger particles have a yellowish or neutral undertone.[9] For this reason, it is important that

[9] The actual diameters of what are described as "larger" and "smaller" particles are not very different from one another. In Chap. 3, we stated that the optimal size of a $TiO_2$ particle to scatter visible light is about 0.25 microns. The average diameter of a typical blue undertone $TiO_2$ sample is roughly 0.23 microns while that of a neutral undertone pigment is roughly 0.26 microns. Despite the small difference in average particle size, the effects on the appearance of the pigment are pronounced.

the $TiO_2$ pigment manufacturer tightly control the particle size for a particular grade of pigment.

In practice, $TiO_2$ undertone is typically measured by dispersing a mix of $TiO_2$ and a black pigment (typically carbon black or black iron oxide) in a suitable medium (for example, silicone or mineral oil) [14]. Once dispersed, the X and Z tristimulus values of the resulting off-gray paste are measured and the ratio of Z/X is calculated. Using standards with defined undertone values, the undertone of an unknown sample is calculated by linear interpolation. Alternatively, the yellowness index of the sample can be determined and used to characterize the pigment [15].

## Summary

Light is modified by a paint through two competing processes—light absorption and light scattering. The sum of these processes determines the opacity of the film, while their balance determines its brightness. The amounts of light absorbed and scattered depend on the details of the paint formulation and the thickness of the applied film.

The absorption and scattering character of a paint can be determined by drawing that paint down on a black and white card at a thickness below that required for complete opacity. The ratio of reflectance values is the contrast ratio of the drawdown. By measuring the wet film thickness, the Kubelka–Munk equations can be used to determine the absorption and scattering coefficients of the paint (K and S). This information can then be used to calculate the effects of changing film thickness, film absorption strength, and film scattering strength on appearance and determine the proper combination of these three parameters to give a complete hide. In addition, the spread rate of the paint—that is, the area that a unit volume of paint can cover at complete hide—can be calculated from these measurements. This is a value of direct importance to paint consumers, since it determines the cost of coverage.

The spread rate, or intrinsic opacity, of a wall paint can be measured as outlined above. In this measurement, it is important that the film be uniformly thick. However, this stipulation is not met by many end-use applications, including wall paints. These paints are typically applied by a brush or roller, each of which results in an uneven, or structured, surface. In these situations, the amount of paint required for complete hide—termed the applied hide of the paint—is greater than that indicated by the spread rate calculated on a uniformly thick paint film.

We can also determine the effectiveness of color pigments to absorb light and white pigments to scatter it by using the Beer–Lambert law. This law relates the amount of light absorbed by a material to the thickness of the material, the light absorption strength of the material, and the concentration of light-absorbing species (for paints, these species are color pigments). By measuring the fraction of light reflected from a thick film of colored paint, we can determine the relative contributions of light absorption and light scattering to opacity. This test, called the tinting strength test, is typically used to compare paints made with different $TiO_2$ pigments or different color pigments. Comparisons of the light reflectance values of a test paint to a control can indicate whether one grade of $TiO_2$ scatters light better than another, or whether one grade of color pigment absorbs light better than another.

Finally, we can use the concepts developed above to characterize the average particle size of a sample of $TiO_2$ pigment. This size characterization is possible because the scattering strengths of different wavelengths of light vary differently with particle size, giving particles of different sizes different undertones. By determining the relative path lengths of red and blue light (done by measuring their ratio, also known as the undertone of the pigment), we can determine if the average particle size of one sample of $TiO_2$ differs from another. As particle size decreases, the scattering strength of blue light is preferentially increased, giving smaller particles a bluer undertone.

## References

1. Kubelka, P., Munk, F.: Ein beitrag zur optik der farbanstriche (A Contribution on the Optics of Paint Layers). Z Tech Phys **12**, 593 (1931)
2. Diebold MP (2014) Application of light scattering to coatings. Springer
3. "Standard Test Method for Hiding Power of Paints by Reflectometry" (2018) ASTM D2805-11
4. "Analytical Colorimetry - Part 2: Saunderson Correction, Solutions of the Kubelka-Munk Equation, Tinting Strength, Hiding Power" (2018) DIN EN ISO 18314-2:2018-12
5. Kubelka P (1948) New contributions to the optics of intensely light-scattering materials. Part I" J Opt Soc Am A 38(**5**):448
6. Judd, D.: Optical specifications of light-scattering materials. J Res Natl Bur Stand **19**, 287 (1937)
7. Mitton PB (1972) "Hiding Power". In: Paint testing, 13th edn. American Society for Testing Materials
8. De Backer S (2019) New method for objective hiding assessment of wall paint. In: Proceedings of the European coatings conference
9. Mitton PB (1972) Mass color and tinting strength. In: Paint testing, 13th edn. American Society for Testing Materials
10. "Standard Test Method for Relative Tinting Strength of White Pigments by Reflectance Measurements" (2017) ASTM D2745-00
11. "Standard Test Method for Determining the Relative Tinting Strength of Chromatic Paints" (2016) ASTM D4838-88
12. "Standard Test Method for Color Development in Tinted Latex Paints" (2013) ASTM D5326-94a
13. Devore, J.R.: Refractive indices of rutile and sphalerite. J Opt Soc Am **41**, 416 (1951)
14. "Standard Test Method for Evaluating the Relative Tint Undertone of Titanium Dioxide Pigments" (2017) ASTM D6131-17
15. "Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates" (2020) ASTM E313-20