Chapter 4
Light Scattering 2—Light Scattering in Crowded Systems

Contents

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Introduction

The complexity of light scattering is significantly greater in crowded systems than in dilute ones (here we define “crowded” systems as those having more than 2.5% volume concentration of TiO_2). In dilute systems, such as those typical of plastics applications, light scattering is proportional to TiO_2 concentration. However, in thin materials, such as paint films, particle concentrations must be proportionally higher than in thicker applications. Due to dependent light scattering, the response of scattering to TiO_2 concentration is not linear at these higher concentrations. The non-linear relationship between opacity and TiO_2 concentration has far-reaching consequences for the coatings industry and understanding light scattering in crowded systems is essential for effective paint formulation.

Similarly, TiO_2 particles are quite crowded in paper applications. Here the root cause is different: papers are generally composed of fibers that are only loosely intertwined. As such, these materials are mostly air, with large gaps (pores) between the fibers. Individual TiO_2 particles are far smaller than these gaps and so are prone to passing entirely through the paper during the wet stage of the papermaking process.

This issue is dealt with in two ways—first, retention aids are added into the process to affix the TiO_2 particles (and extender particles) onto the fiber surfaces. Second, the TiO_2 particles are intentionally flocculated into clusters (often hetero-clusters that include extender particles) that are large enough to be trapped by the fibers. Because of this, even though the volume concentration of the TiO_2 pigment may be low, the particles are crowded to the same extent as in highly concentrated paints. This is discussed in more detail in Chap. 18.

Our primary focus in this chapter is light scattering in paint systems. Many of the principles that are discussed here are demonstrated using paints that were developed solely for this purpose and without regard to other important paint properties. As such they are not meant to represent paints that would be suitable for commercial or practical purposes. The practical aspects of formulating such paints are discussed in detail in Chap. 16.

Particle Volume in Paints—The PVC

Many important properties of paints, plastics, and papers are determined by the concentrations of the particles they contain. An important aspect of these concentrations is the way in which we measure them—on a weight basis, a volume basis, or something else. As a practical issue, using weight to define concentration is very convenient as we can measure weight directly and, in most types of manufacturing, we use weight to indicate how much of an ingredient to add to a production batch. However, when considering the properties of a material containing particles, it is often the volume of the particles that determine their effect on properties, rather than their weight. This is especially true in paint applications, where the particles typically occupy a significant portion of the paint film volume. For this reason, we quantify the concentrations of particles in paint films on a volume basis.

Measuring Particle Concentration

There are two separate aspects of the volume concentration that are important to paint properties. The first has to do with the balance between the volume of resin and the volume of particles. Resin holds the particles together and attaches them to the substrate, and paints with similar balances between resin volume and particle volume often have similar mechanical and physical properties. For example, replacing one extender with another will normally result in similar paint properties if the replacement is done on an equal volume basis rather than an equal weight basis.[1]

The second reason we use volume to characterize concentrations in paints is that the scattering strength of TiO_2 particles decreases with decreasing surface-to-surface distances. This is because, as we saw in Chap. 3, the scattering volume of a TiO_2 particle is significantly greater than its physical volume. The fact that the scattering volume is much larger than the physical volume increases the total scattering strength of a particle considerably. However, at even modest concentrations of TiO_2, the particles are close enough together for their scattering volumes to overlap. This decreases the total scattering volume of the system and can be interpreted as a loss of TiO_2 scattering strength. As we will see, the rate of decrease in particle scattering strength is nearly constant with increasing concentration, and so volume concentration tells us how strongly the particles scatter light.

By contrast, in plastics applications, we typically use weight percent (also called "hundred weight" or "pounds per hundred"—pph) to characterize particle content. This is because at the low concentrations of TiO_2 that are typical of plastics applications (less than one volume percent), scattering loss due to scattering volume overlap is negligible. That is, the change in scattering loss with concentration, which makes the TiO_2 volume percent important in paints, is not an issue for plastics. In addition, particles are bought, sold, and used on a weight basis. Taken together these considerations support the use of weight as the basis for particle concentrations in plastics.

Particle concentrations measured on a volume basis are termed "pigment volume concentrations" and abbreviated as PVC. It is unfortunate that the word "pigment" is used here, rather than the word "particle", because this concentration is, in fact,

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[1] Of course, the two are the same if the density of the particles are the same. This is true when replacing, for example, a calcium carbonate extender with one particle size with a calcium carbonate extender of another.

determined by the amounts of all particles, not just the pigment particles,[2,3] PVC is typically given as a percentage from 0 to 100, with the percent sign (%) omitted, but is occasionally given as a fraction from 0 to 1. It is usually clear from context which convention is being used.

The calculation of the overall PVC for a dry paint film is straightforward, as shown in Eq. 4.1. Because TiO_2 alone scatters light effectively, we often wish to calculate its relative volume separately. This quantity is called the TiO_2 PVC, and its calculation is shown in Eq. 4.2. When the particle concentration is low, the particles are said to be dilute, while, when it is high, they are said to be concentrated or crowded.

$$PVC = 100x \frac{(extender\ volume) + (TiO_2 volume)}{(extender\ volume) + (TiO_2\ volume) + (resin\ volume)} \tag{4.1}$$

$$TiO_2PVC = 100x \frac{TiO_2\ volume}{(extender\ volume) + (TiO_2\ volume) + (resin\ volume)} \tag{4.2}$$

Notice that in both equations the denominator is not the total volume of the paint film, but rather the combined volumes of the pigment, extender(s), and resin. In most paints, these combined volumes are, in fact, the total volume of the paint film. However, in paints that incorporate air pores for hiding purposes, we do not include the air volume in the PVC calculation. The implications of this are far reaching, as will be discussed later in this chapter.

The pigment-to-binder ratio (P/B) is sometimes used in the paint industry as an alternative to the PVC. This is a weight-based value that is defined as the mass of the pigments and extenders divided by the mass of the dried binder, and expressed as a fraction. Although the P/B ratio is a bit easier to calculate, we prefer to work with PVC as this is based on the physically more relevant volume composition of the film rather than the weight composition. The P/B ratio and PVC are related through Eqs. 4.3 and 4.4:

$$PVC = 100\text{ x } \frac{1}{\frac{\vartheta}{\mathrm{P}/\mathrm{B}} + 1} \tag{4.3}$$

$$\mathrm{P}/\mathrm{B} = \frac{\vartheta}{\left(\frac{100}{PVC}\right) - 1} \tag{4.4}$$

where ϑ is the ratio of the particle density to the resin density. If more than one type of particle is present, their weight average density is used in these equations.

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[2] The origin of the term PVC dates to a time when it was common to call all particles added to a paint, including extender, “pigment”. Today we restrict the word “pigment” to those particles that interact with light.

[3] It is also unfortunate that “PVC” is often used as the acronym for polyvinyl chloride, a plastic used in high volumes worldwide.

The Critical Pigment Volume Concentration (CPVC)

The PVC tells us about the balance between the resin and particle contents. While the PVC concept appears straightforward, there is an important aspect of it that is somewhat complicated. This aspect is that above a certain PVC value—the critical PVC or CPVC—a third component enters the paint film: air.

Before discussing the implications of the air regarding the way that we view particle concentration, we will first describe how it is brought into the film through the following thought experiment. We begin with a cube, 100 microns on a side, that is filled with resin. The starting PVC is obviously zero, since there are no particles. Next, we wish to increase the PVC of the cube. We cannot do this by simply adding particles to the cube because the cube is already filled with resin. Instead, we must remove resin to make room for the added particles, that is, we must replace resin with an equal volume of particles. For our purposes, we will assume that the particles are added at random locations within the cube. If necessary, we will rearrange the particles already in the cube to create contiguous regions of resin large enough to accommodate new particles.

We can make these replacements, with the necessary particle rearrangements, only up to a point. At some concentration of particles, we find that while there is still resin present in the cube, no amount of particle rearrangement can create a region of pure resin that is large enough to fit an added particle. This concentration is the CPVC. At this concentration, there is just enough resin to coat each particle with a monolayer of resin and to fill the voids between the particle with resin [1]. We call the amount of resin needed to reach this state the "resin demand" of the particles.

We might expect the CPVC to be the upper limit of PVC, since no more particles can be fit into our 100 micron cube and so we cannot increase their concentration. This expectation is not correct, however. We can continue to increase the PVC because the PVC calculation uses only the volumes of the particles and the resin. We can continue to remove resin, while holding the particle concentration constant, by replacing resin with air. That is, we can continue to increase the PVC, as defined in Eqs. 4.1 and 4.2, by changing our thought experiment at the CPVC point from replacing resin with particles to replacing resin with air. The many implications of this change in our thought experiment are important and far reaching, as will be made clear below, but here we will observe that many of the properties of the paint film experience a discontinuity at the CPVC. Before discussing the implications of replacing resin with air, rather than with particles, we will consider two alternatives to use the PVC to express particle concentrations in systems above the CPVC.

The first of these is the pigment packing factor, ϕ. This value gives the concentration of particles based on the entire volume of the paint film (or the volume of the cube in our thought experiment), including air, rather than the combined volumes of just the particles and resin. This calculation is shown in Eq. 4.5, which is similar to Eq. 4.1 except that the volume of air (when present) is included in the denominator. Unlike PVC, ϕ is typically reported as a fraction (from 0 to 1) rather than percentage. The pigment packing factor is identical to the PVC in paints below the

CPVC. Importantly, however, at and above the CPVC, the pigment packing factor is constant because we can place no more particles into our cube (i.e., neither the numerator nor the denominator of Eq. 4.5 change above the CPVC).

$$\phi = \frac{(extender\ volume) + (TiO_2\ volume)}{(extender\ volume) + (TiO_2\ volume) + (resin\ volume) + (air\ volume)} \tag{4.5}$$

The invariance of the pigment packing factor above the CPVC is an indicator of an important change that occurs at the CPVC. Below the CPVC, when we add particles, we increase their absolute concentration and so increase the degree of crowding (and the scattering volume overlap) that they experience. However, above the CPVC, particle crowding no longer increases. This means that there is no further increase in scattering volume overlap and so no further decrease in scattering strength as the PVC increases. That is, while more particles are present (the PVC is higher), the particles are no more crowded than at the CPVC. This seeming contradiction is explained by the total volume of the paint film being increased when air is added, while the combined volume of the particles and resin is held constant throughout. This will be explained in more detail later in this chapter.

The second alternative to the use of PVC to characterize particle concentrations is the reduced PVC. As we will see, paints do not all have the same CPVC value and, in fact, the CPVC values of two paints can differ by a significant amount. When comparing the properties of paints that differ in CPVC value, it is found that many paint properties are comparable when the degree to which the paints exceed (or, alternatively, are lower than) the CPVC is similar. This degree can be conveniently described by the reduced PVC, which is the ratio of the actual PVC to the CPVC and is typically indicated by the symbol Λ. The reduced PVC is less than one below the CPVC and greater than one above it.

Particle Packing in Crowded Systems

Random packing of uniformly sized macroscopic spheres, for example, glass marbles or tennis balls, typically results in a volume density (CPVC) within the narrow range of 64 ± 2% [2]. By contrast, the packing density of particles found in paints, when at their CPVC values, span a much greater range, with values both above and below that of uniformly sized macroscopic spheres. There are three contributors to this difference in packing behaviors at the macroscopic and microscopic scales.

The first contributor is the relatively high attraction and frictional forces between small particles compared to their macroscopic counterparts. As described in Chap. 1, the packing of these particles in air is quite loose because their high surface areas give them high internal friction that “freezes” the particles in place and prevents the particles from settling or compressing into a denser state. The magnitude of this effect in air is such that the void fraction of nanosized particles can exceed 99%. A similar effect is seen when nanosized particles are packed in oil or resin, although to a lesser extent. As an example, nanoparticles of aluminum hydroxide (0.01 to 0.30 microns) have CPVC values from 13.0 to 33.2 [3].[4] Another way of saying this is that small particles have a high resin demand, and so a low CPVC value.

A second physical factor that can affect the CPVC of a particle is the particle shape. Packing efficiency generally increases when going from needles to plates to blocks. In addition, nanosized particles have associated with them a degree of "structure". This term applies to aggregates of these particles and refers to the openness of the three-dimensional arrangements of these particles. Quite often small particles form linear or spikey aggregates that cannot pack efficiently and so have low CPVC values. Examples of particles for which structure is important are fumed silica and carbon black, both of which have very low CPVC values (below 20).

Both frictional forces and a high degree of structure result in an open, low CPVC packing arrangement. By contrast, the third factor that affects CPVC, non-uniform particle size, results in a denser packing arrangement than is possible with densely packed, uniformly sized particles. This situation arises when a single particle type has a very broad particle size distribution or when two or more particle types with different particle diameters are mixed.

To demonstrate this principle as it applies to paints, we will first discuss the effect of multiple particle sizes on packing density in two dimensions. We begin by considering a field containing circles of diameter 10 units that are packed closely together (Fig. 4.1a). For closest packed arrangements of uniformly sized circles, the area coverage is 91%, but with the looser packing in Fig. 4.1a, the circles cover 75% of the area. Next, we place smaller circles (diameter 2 units) between the larger ones (Fig. 4.1b). These circles occupy 11% of the field, bringing the total area covered by all circles to 86%. Finally, we place still smaller circles (diameter 0.75 units) in the remaining void areas. This further increases the coverage to 93%, that is, the field is filled with loosely packed circles of three different sizes to a greater extent than is possible with efficiently packed circles of only one size.

The same principle applies to the filling of three-dimensional volumes. We can increase the CPVC of a particle mix by using particles of different sizes and nesting the smaller particles in the regions between the larger particles. This is demonstrated in Fig. 4.2, which shows the CPVC values of large extender particles (10 microns), small extender particles (0.55 microns), and mixtures of the two [4, 5]. Because small particles can displace resin in the regions between large particles, the total volume concentration of the particles in these mixtures (that is, their CPVC) can be greater than that of either particle packed efficiently by itself.

Note also that the CPVC value for the small particles (PVC = 41.6) is significantly reduced from the CPVC value of the large particles (PVC = 50.1), in accordance

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[4] These values were determined by oil absorption measurements made using dioctyl phthalate oil (DOP) rather than linseed oil, which is used in a typical oil absorption test, as discussed later. This is relevant because DOP has a higher density (1.05 g/ml) than linseed oil (0.93 g/ml).

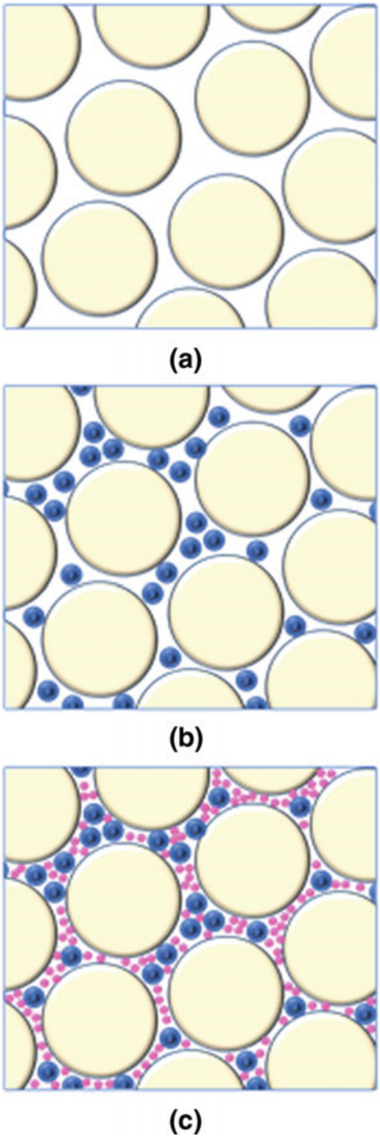

Fig. 4.1 Increasing maximum coverage by nesting circles of different sizes

with the first two reasons for CPVC to vary that are outlined above. In addition to these reasons, particle surfaces are coated with a thin layer of resin, and the higher surface areas of small particles require more of resin to satisfy this need and so lowers the CPVC. This will be discussed in detail later in this chapter.

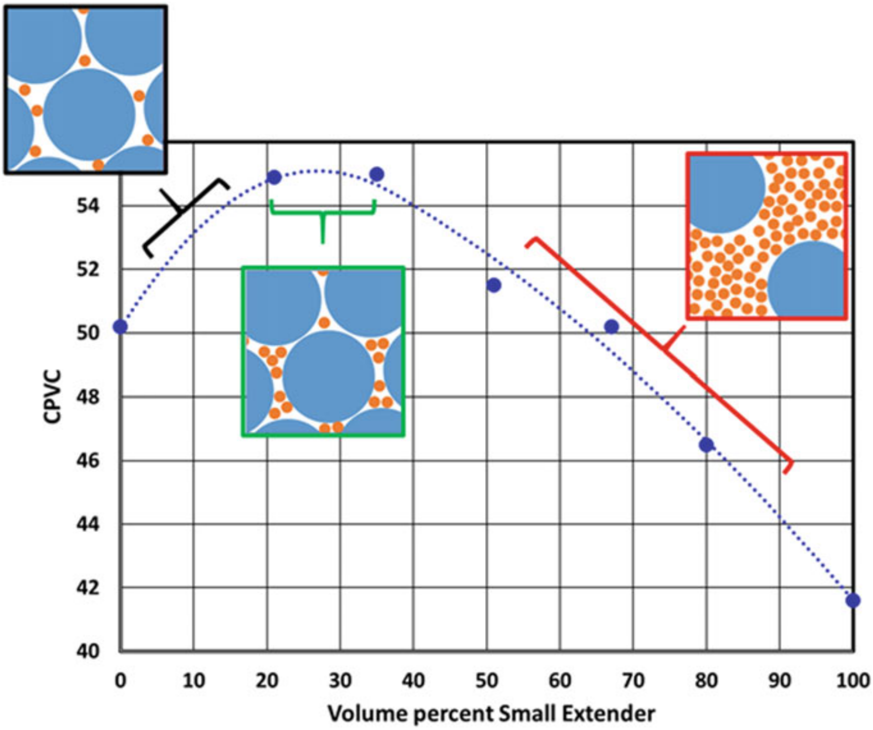

Fig. 4.2 Critical pigment volume concentrations of a large extender particle (10 microns), a small extender particle (0.55 microns), and mixtures of the two. Adapted from [4, 5]

The Opacity Versus PVC Curve

The relationship between a paint's composition and its opacity is complicated by fact that the scattering volume overlaps between TiO_2 particles, and with it their scattering strengths, are dependent on the concentrations of both the TiO_2 particles and the extender particles.[5] A practical way of addressing the formulation complexity that this causes is through a graph of paint opacity as a function of TiO_2 PVC. To use this graph as a formulation tool, we must first discuss the factors that determine it.

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[5] Note that there is not a scattering volume overlap between TiO_2 particles and extender particles in contact with one another since the scattering volume of an extender particle embedded in a resin does not extend outside of its physical volume, due to it having a similar refractive index to that of the surrounding resin.

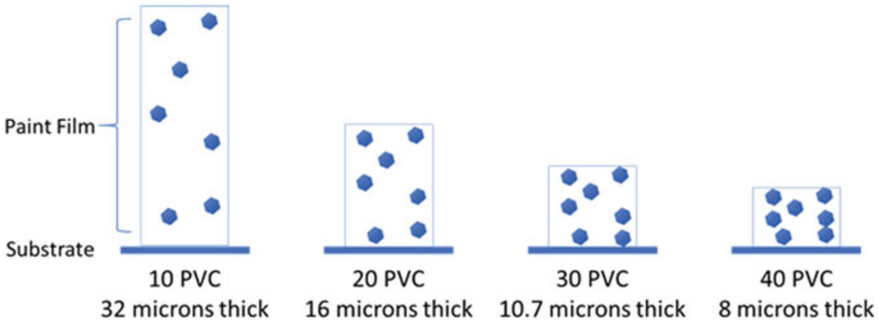

Fig. 4.3 Relationship between PVC and dry thickness for the paints shown in Fig. 4.4

Visualizing the Loss of Scattering Efficiency Due to Dependent Light Scattering

As was shown in Chap. 3, when the TiO_2 PVC exceeds about 2.5, the surface-to-surface distances between neighboring particles are small enough that even in an ideally spaced arrangement, the scattering volumes of the particles begin to overlap.[6] The detrimental effect of scattering volume overlap on paint opacity above this TiO_2 PVC can be seen visually in the following experiment: a series of paints were made at different TiO_2 PVC values and applied to black and white opacity charts at different film thicknesses. These thicknesses were chosen such that the total number of TiO_2 particles applied per square centimeter of dry film was the same (Fig. 4.3). Two grades of TiO_2 were investigated—a universal grade and a highly treated grade that is typically used in paints formulated above the CPVC (such paints are discussed in detail in Chap. 16).

Images for these two paint drawdown series are shown in Fig. 4.4. In both series, the opacity declines significantly as TiO_2 PVC increases, even though the same number of scattering centers cover each drawdown chart.

Close inspection of Fig. 4.4 shows that opacity generally decreases as TiO_2 PVC increases, as expected based on crowding arguments. However, there is a reversal of this trend at the highest PVC values for both paint series (the highest PVC paint made with the universal grade, and the three highest PVC paints made with the highly treated grade). This is due to these films being above the CPVC value for these pigments.[7] As such the films contain air voids that, as will be discussed in a later section of this chapter, are capable of scattering light on their own and also increase the scattering strength of the TiO_2 particles.

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[6] Even below this PVC, scattering volume overlap typically occurs in paints because the particle arrangement is closer to random than to ideal, and so particles can, by chance, be close to one another.

[7] The significance of the difference in CPVC value for the highly treated grade (approximately 45) and the universal grade (approximately 60) will be discussed in Chap. 16.

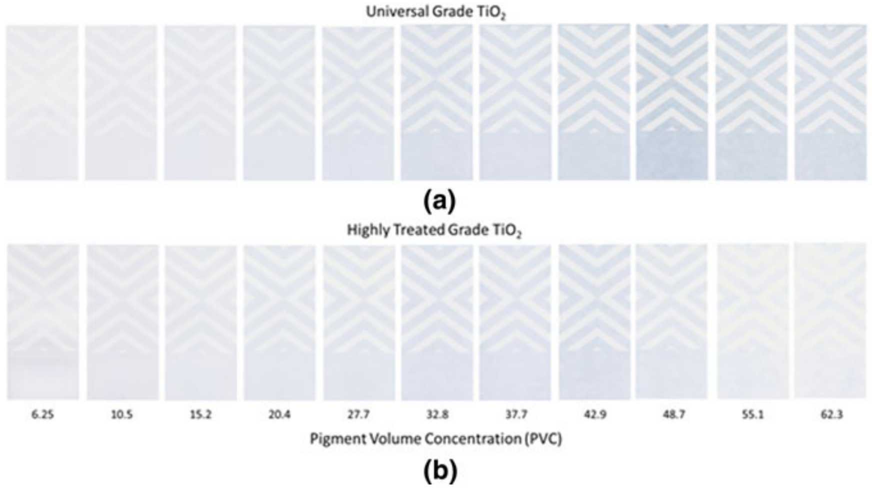

Fig. 4.4 Effect of TiO_2 crowding on paint opacity for two grades of TiO_2 pigment. Each film has the same number of TiO_2 particles per square centimeter. **a** Universal TiO_2 grade. **b** Highly treated TiO_2 grade

Quantifying the Loss of Scattering Efficiency Due to Dependent Light Scattering

The effect of TiO_2 PVC on film opacity is complex, since increasing the TiO_2 PVC increases the number of scattering centers, but at the same time reduces the scattering strength of these centers by increasing scattering volume overlap. To determine the overall effect of those opposing factors, we can experimentally measure the average scattering strength per TiO_2 particle as a function of PVC.[8]

The results of one such experiment, in this case a laboratory paint system,[9] are shown in Fig. 4.5. We see that the scattering strength of the TiO_2 particles decreases linearly with increasing particle concentration, and that the rate of decrease is relatively steep—the consequences of dependent light scattering can be quite significant between the two ends of the range of TiO_2 PVC values typically seen in paints (roughly 8 to 25). The scattering power difference is about 30%. Extrapolating this line to higher PVC values, we calculate that at the CPVC of this paint system (41.5), the total loss of scattering power is 75% compared to isolated TiO_2 particles.

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[8] We do this by first measuring the scattering strength of an entire paint film (see Chap. 13), and then dividing that by the number of particles in the paint, using PVC as a proxy for the number of particles.

[9] We define a paint system as a series of paints, made with the same particle or particle mix, that spans a range of PVC values.

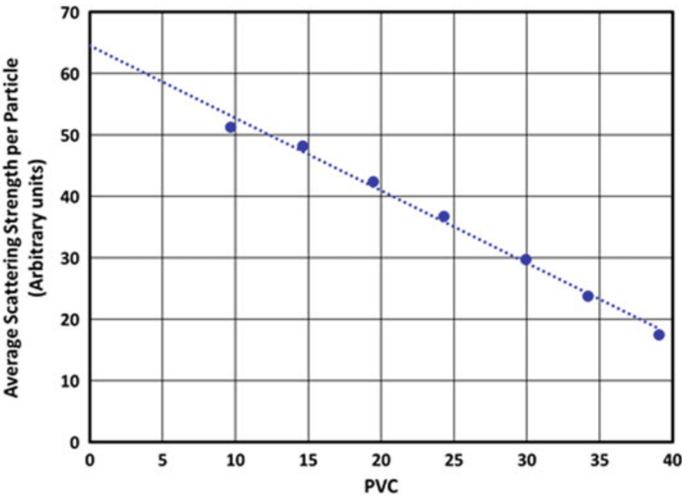

Fig. 4.5 Scattering strength per particle for a series of paints made at different PVC values using the same resin and TiO_2 pigment

Factors Affecting the Rate of Scattering Strength Loss at Increasing PVC Values

Studies similar to that shown in Fig. 4.5 for different paint systems reveal that the loss of scattering strength line varies according to the exact nature of the paint system. Some of the more important paint parameters that affect this relationship are the size of the resin particles, the amount of coalescing agent, the grade of TiO_2 pigment, and the size and concentration of any extender particles. This variability is shown for three pairs of paint systems in Fig. 4.6.

In the first pair of paint systems (Fig. 4.6a), the paints have the same grade of universal TiO_2 but differ in the size of the resin particles (the resin particles have the same chemistry). The second pair (Fig. 4.6b) shows paint systems made with the same universal grade of TiO_2 as in Fig. 4.6a, but with a different resin than the paints in Fig. 4.6a. In one case, TiO_2 is the only particle present while in the other a constant amount (15 PVC) of a 15 micron extender is also present. Finally, in the third pair (Fig. 4.6c), two types of TiO_2 pigments are compared (the same universal grade as shown in Fig. 4.6a, b, and a highly treated grade) in the same resin system as shown in Fig. 4.6b. Note that the blue lines in Fig. 4.6b, c are the same.

As is true for any line, those shown in Fig. 4.6 have two independent parameters—the y-axis intercept and the slope. Each of these is a direct measure of an important opacity attribute of the paints. The first, the y-axis intercept, is the scattering strength of an isolated TiO_2 pigment particle (that is, of a single particle for which there is no reduction in scattering volume due to the presence of close neighbors). We will refer to this as the intrinsic scattering strength of the particle.

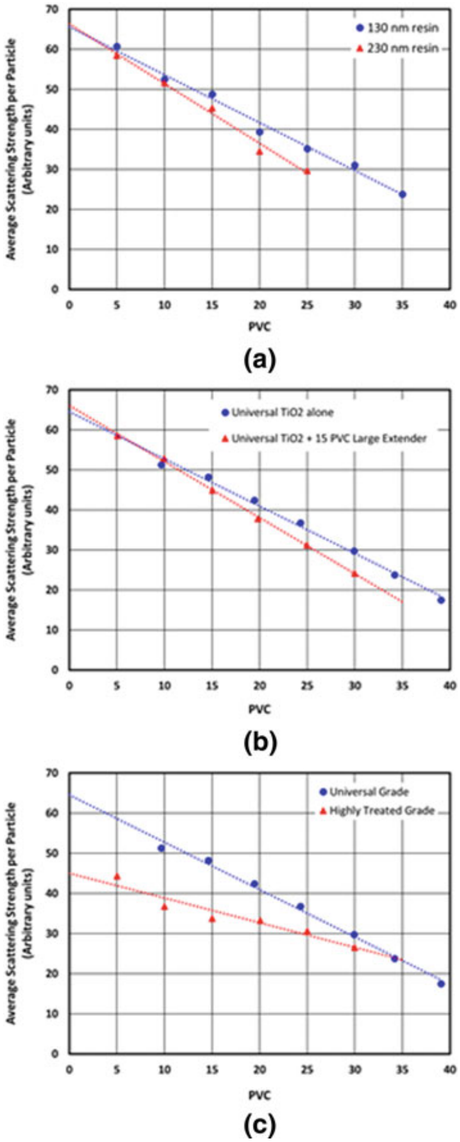

Fig. 4.6 Average TiO_2 particle scattering strength as a function of PVC. **a** Universal TiO_2 pigment incorporated into paints with two different sizes of resins. **b** A universal TiO_2 pigment alone and with 15 PVC large extender. **c** Two different grades of TiO_2 pigment in the same paint as shown in (**b**)

We would expect that the intrinsic scattering strength of the TiO_2 particles to vary from one pigment grade to another, but to be independent of other aspects of the paint system (resin, extender, etc.). This should be the case for the four paint systems in Fig. 4.6a, b, since these are all made with the same universal grade of TiO_2. The lines for these paints are plotted together in Fig. 4.7, where we see that the y-axis intercepts (i.e., the intrinsic TiO_2 scattering strengths) for all four paint systems are, as expected, very nearly the same.

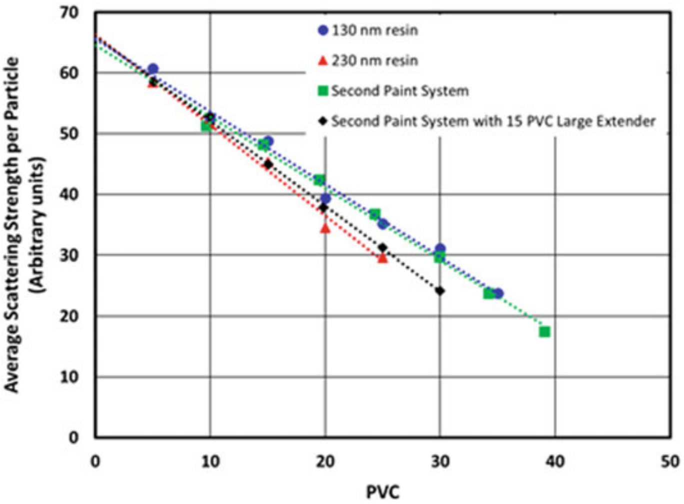

Fig. 4.7 Average scattering strength per particle for the same universal grade of TiO_2 in four different paint systems

The second parameter of the lines shown in Fig. 4.6—their slope—is a measure of the degree to which scattering volume overlap increases with increasing TiO_2 concentration in the different paint systems. In the absence of scattering volume overlap, the slopes of these line would be zero and the line would be horizontal. When we compare the slopes of the lines in Fig. 4.6, we see that in some paint systems the TiO_2 scattering strength decreases more rapidly with PVC than in others. For example, in Fig. 4.6a, b, we see that the presence of large particles (either resin or extender) results in a more rapid loss of scattering power (this can be seen more directly in Fig. 4.7). This is expected based on the crowding effect that large particles have on TiO_2 particle spacing, as discussed earlier.

In Fig. 4.6c, we see that the intrinsic scattering strength of the universal pigment is significantly greater than that of the highly treated TiO_2 grade. We also see that the particles of the universal TiO_2 grade lose scattering strength more rapidly than do those of the highly treated grade. We will defer a more detailed discussion of these grades to Chap. 7, but here we note that these observations can be understood based on two important differences between these grades. First, as the name implies, the heavily treated grade has more surface treatment than the universal grade, and so a lower TiO_2 content (that is, there are fewer TiO_2 particles per kilogram of pigment). The reduced TiO_2 content of the pigment particles results in a reduction of their intrinsic scattering strength as particle concentration increases (i.e., their y-axis intercept).

Second, this heavy coating prevents the TiO_2 cores of the pigment particles from coming very close together (this is, in fact, its purpose). Because the surface coating acts as a barrier, preventing the close approach of the TiO_2 cores, it reduces the loss in opacity due to scattering volume overlap as the particle concentration increases.

The line for this grade, therefore, is less steep than that of the universal grade. In this case, it is roughly half as steep, indicating a nearly 50% reduction in the rate of loss of scattering strength.

Making the Opacity Versus PVC Curve

Figure 4.5 shows the average scattering strength of a TiO_2 particle as a function of TiO_2 concentration for a laboratory paint system. While this information can be of great use to the paint formulator, paint consumers have little interest in the average scattering strength of a single particle. Their interests instead lie in the combined scattering of all particles, that is, the total scattering strength, or opacity, of the entire film.

The scattering strength of the entire film is simply the scattering power of an average TiO_2 particle (Fig. 4.5) multiplied by the number of particles in the film. It would be tedious to calculate the actual number of particles, so instead we multiply the scattering strength per particle by the TiO_2 PVC, which varies linearly with the number of particles. Doing this for the data points in Fig. 4.5 gives the curve in Fig. 4.8—the opacity versus PVC curve. This curve is among the more powerful tools available to the formulator of TiO_2-containing paints.

There is a sharp discontinuity of this curve at a PVC value of 41.5. This is the CPVC for this particular paint system. As was discussed in our thought experiment describing the process of increasing the PVC of a 100 micron cube of paint film, the

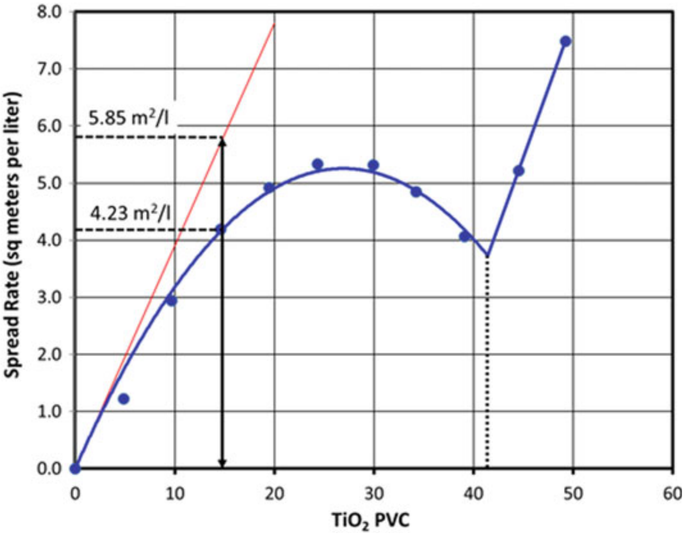

Fig. 4.8 Opacity versus PVC curve for a paint containing only resin and a universal grade of TiO_2. This is the same paint formulation as used in Fig. 4.5

way PVC is increased below the CPVC is very different than the way it is increased above the CPVC—below the CPVC, resin is replaced with particles, while, above the CPVC, it is replaced with air. In that discussion we stated that this change in the thought experiment results in a sharp change in many paint properties at the CPVC point. Clearly film opacity is one of these properties.

There are many ways to characterize the scattering strength, or opacity, of a paint film. In opacity versus PVC charts, it is often convenient to do so using the spread rate of the paint, which is defined as the number of square meters that a liter of paint can cover at complete hide.[10] The benefit of using spread rate is that it directly displays the property of direct interest to the paint consumer, namely, how much paint is required for a specific job.

In practice, we construct the opacity versus PVC curve by measuring the spread rates of a series of white paints that are identical except for their TiO_2 PVC.[11] This is most easily done by first making large amounts of master paints at the two ends of the concentration range of interest and blending them in the appropriate ratios to give the target intermediate concentrations. If extenders are anticipated in the final formulation, they can either be held at a constant level throughout the paint series or varied in proportion to the paint PVC (that is, by using a constant ratio of TiO_2 and extender throughout the series). In addition, it is best (but not essential) that all the paints have the same volume percent solids. A bar chart representation of the relative volumes of the water, resin, and TiO_2 for the series of waterborne paints used to construct Figs. 4.5 and 4.8 is shown in Fig. 4.9a.

Next the paints are applied to black and white opacity cards (as shown in Fig. 4.4). Reflective measurements are made over the black and white backgrounds, and spread rate is calculated using the procedure in Chap. 13.

While not strictly necessary, it is conceptually easiest to consider the paints to have been drawn down at the same wet film thicknesses. This results in the combined volume of pigment and resin being the same for each dry film (Fig. 4.9b). The dry film thicknesses for paints below the CPVC are identical, while above the CPVC the thickness increases linearly with PVC.

The monotonic increase in the height of the orange bars in Fig. 4.9b indicates that the TiO_2 coverage rate, measured as, for example, the grams of TiO_2 per square meter, increases linearly with PVC. The reason for this linear relationship below the CPVC is obvious—the same solids are applied per unit area, and so the amount of TiO_2 per unit area will increase proportionally with the TiO_2 PVC. However, it is less obvious as to why this increase should continue to be linear with PVC, and why the rate of increase is the same above the CPVC as below.

We can understand this by returning to our thought experiment in which we sequentially replaced the resin in a 100 micron cube side with TiO_2 particles. Below the CPVC, the increase in TiO_2 coverage rate is simply due to an increase in the

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[10] Most commercial paints have spread rate values greater than the laboratory paint used to generate Fig. 4.8. However, the laboratory paint was not optimized to give high levels of opacity, but rather was developed to best exemplify the concepts discussed here.

[11] The procedure for measuring the spread rate of a paint is given in Chap. 13.

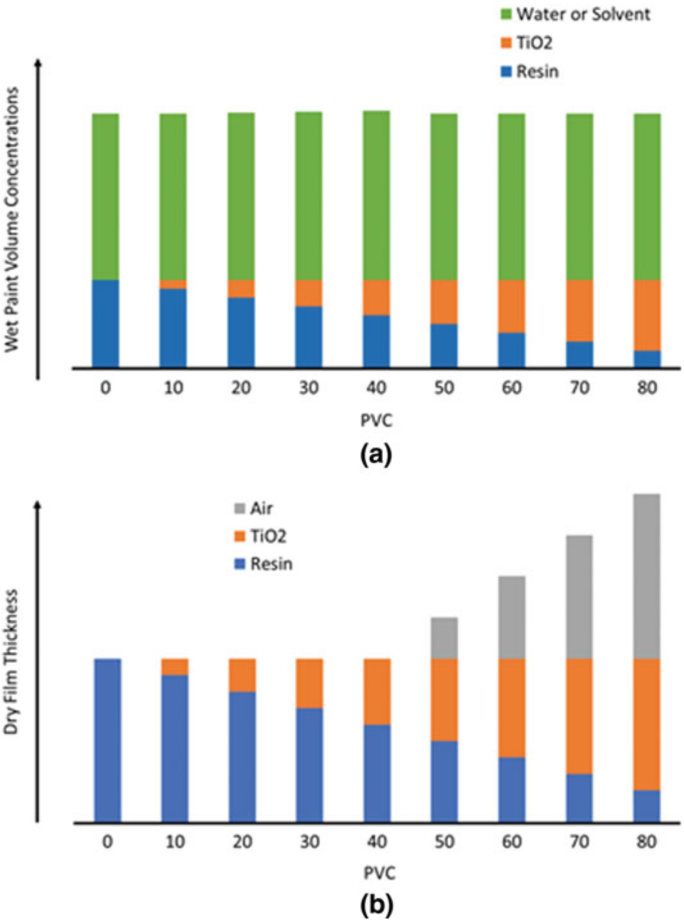

Fig. 4.9 Relative proportions of **a** wet paint and **b** dried paint film for a PVC paint series. The CPVC for this paint is 41.5

number of TiO_2 particles in the cube. However, once we reach the CPVC value, we can no longer increase the number of TiO_2 particle in the cube, and so it seems that an increase in TiO_2 coverage with increasing PVC is no longer be possible. However, as shown in Fig. 4.9b, the volume of dry paint—that is, the number of 100 micron cubes in the film—increases above the CPVC due to the increase in dry film thickness (which, in turn, is due to the increase in air volume in the dry film). The increase in the number of cubes occurs at a rate exactly such that the relationship between the TiO_2 PVC and the TiO_2 coverage rate continues unabated as the paints pass across the CPVC threshold.

Significance of the Curve Maximum

The significance of the PVC of the maximum in the opacity curve (PVC = 27.1 in Fig. 4.8) has often been confused both in the literature and in the coatings industry as a whole. It does indicate, of course, a maximum for some parameter of the paint system. This parameter is often claimed to be the PVC at which the TiO_2 scatters light most efficiently. This is in error—in Figs. 4.5 and 4.6 we saw that the scattering efficiency of a TiO_2 particle is highest at very large dilution (PVC close to zero) and decreases monotonically as the PVC is increased. Alternatively, it has been suggested that this maximum signifies the PVC for which the cost of the paint, on a coverage basis, is the lowest. This, too, is in error as the PVC for minimal cost of coverage is dependent not only on the shape of the curve but also on the relative costs of the resin and TiO_2 pigment, which do not enter into Fig. 4.8 [6].

The parameter being maximized in Fig. 4.8 is, in fact, the scattering efficiency of the entire film on a thickness basis, that is, the maximum in Fig. 4.8 gives the PVC for this paint system that gives the greatest hiding for a set thickness of film. This is an important consideration in many thin film paint applications, where only a limited amount of film is either desired or capable of being applied to the substrate. These paints should be formulated at the PVC that gives a maximum in the curve.[12]

Curve Shape Below the CPVC

The opacity versus PVC curve is an extremely useful tool for the paint formulator as it can reveal the effects of different aspects of a paint (TiO_2 grade, resin, extenders if present, etc.) on film scattering strength. This is done through a careful analysis of various aspects of the curve, both from a mathematical viewpoint and a physical viewpoint.

Mathematical Analysis

We will begin our analysis from a mathematical perspective and derive from this the expected shape of the curve below the CPVC (i.e., in the absence of air void scattering). To do this, we will return to our earlier description of the points on this curve as being calculated by multiplying, at each PVC value, the scattering power of an average particle at that PVC, by the number of particles at that PVC.

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[12] Most paints are formulated at lower PVC values than the maximum in this curve for cost reasons—even though a lower PVC film must be thicker than the film at the PVC for the maximum in this curve, the TiO_2 in the film, by being at a lower PVC value, scatters light more efficiently and so less TiO_2 is required per unit area covered at complete hide.

From Fig. 4.5, we see that the scattering power of an average particle decreases linearly with increasing TiO_2 concentration. We can represent this with Eq. 4.6:

$$\text{Scattering per particle} = \mathrm{a} \cdot (\mathrm{PVC}) + \mathrm{b} \tag{4.6}$$

As discussed when Fig. 4.5 was introduced, the slope of the line ("a" in Eq. 4.6) represents the rate of scattering loss as particle concentration increases. Because scattering power decreases with increasing PVC, the value of "a" is negative.

We can also write an equation for the number of particles in the paint as a function of the paint PVC:

$$\text{Number of particles} = \mathrm{c} \cdot (\mathrm{PVC}) \tag{4.7}$$

The number of particles, obviously, increases with increasing PVC, and so "c" in Eq. 4.7 is a positive number. Since there are no particles present when the PVC value is zero, there is no constant in this equation that would be analogous to the "b" term in Eq. 4.6.

To determine the total scattering strength of the paint film, we simply multiply the scattering power of an average particle by the number of particles:

$$\begin{aligned}\text{Total scattering} &= (\text{scattering per particle}) \times (\text{number of particles}) \\ &= (\mathrm{a} \cdot \mathrm{c})(\mathrm{PVC})^2 + (\mathrm{b} \cdot \mathrm{c})(\mathrm{PVC}) \end{aligned} \tag{4.8}$$

Since Eqs. 4.6 and 4.7 are first order in PVC, their product (Eq. 4.8) is second order in PVC. That is, the total scattering (opacity) versus PVC curve is expected to be parabolic [7] as Fig. 4.8 shows it to be. Because there is no constant in Eq. 4.8 (or, more precisely, because the constant is zero), this function passes through the origin of the graph. The physical significance of this is that there is no film scattering when there are no particles present, which is a reasonable boundary condition to set for this curve. In addition, because the coefficient of the second-order term ("a·c") is negative, the parabola will face downward.

A second-order equation generally has associated with it three independent parameters—the coefficient of the second-order term ("a·c" in Eq. 4.8), the coefficient of the first-order term ("b·c" in Eq. 4.8), and a constant term (zero in this case). We saw that the constant term being zero had a physical significance; this is also true of the two other coefficients in this equation. The magnitude of the coefficient of the second-order term ("a·c") determines the degree of curvature of the parabola. When this coefficient is small, there is little curvature and the curve takes on a near-linear appearance.

The final parameter in a second-order equation—the coefficient of the first-order term (b·c in Eq. 4.8)—determines the location of the maximum of the curve (in terms of both the x-value and y-value at the curve maximum). When the other two parameters of Eq. 4.8 (the constant and the coefficient of the second-order term) are set, as they are here, the PVC of the maximum in the curve and the scattering power at this maximum cannot be set independently—instead they are linked through the coefficient of the first-order term.

The shape of the curve at low PVC values has important implications to materials with low concentrations of light scattering particles (such as most plastics). At low PVC, the second-order term in Eq. 4.8, ((a·c)$(PVC)^2$), is quite small compared to the first-order term, ((b·c)(PVC)), and the curve in the vicinity of the origin is nearly linear. For this reason, the response of total scattering to PVC in most plastics applications, where the PVC value is quite low, is nearly linear. This is a mathematical restatement of the reason given for this earlier (that the surface-to-surface distances at low PVC values remain so large that there is very little increase in scattering volume overlap as the PVC increases).

Examples of Opacity Versus PVC Curves

We saw in Fig. 4.6 that several parameters of a paint system can affect the relationship between TiO_2 scattering strength and PVC. In Fig. 4.10, we show the opacity versus PVC curves that are generated from the lines in Fig. 4.6.[13] As can be seen, these curves differ in (1) the tangent at the origin (shown as dotted lines in Fig. 4.10), (2) the degree of curvature below the CPVC, (3) the PVC of the curve maximum (i.e., the x-value at the maximum), (4) the spread rate at the curve maximum (i.e., the y-value at the maximum), (5) the CPVC value, and (6) the rate of opacity increase above the CPVC. In the previous section, we discussed the relationship between the first four of these differences and the mathematical equations describing these curves. We discussed the fifth difference—the PVC value of the CPVC—in the section on particle packing, and we will discuss the sixth difference—the shape of the curve above the CPVC—in the section on opacity above the CPVC.

Quantifying the Opacity Loss Due to Scattering Volume Overlap

Returning to Fig. 4.8, the straight red line is the tangent of the curve at the origin. This line shows what the response of spread rate to increasing TiO_2 concentration would be if there were no reduction in TiO_2 scattering strength due to scattering volume overlap. We can use this red line to calculate scattering power loss due to scattering volume overlap. We see, for example, that the spread rate of the 15 PVC paint would be 5.85 m^2/l in the absence of scattering volume overlap while the measured spread rate is only 4.23 m^2/l. This represents a scattering power loss of nearly 28%. At the CPVC, the reduction in scattering strength is 77%. Clearly no commercial paints

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[13] In actual practice, the order of these steps is reversed—first we measure the opacity of the paint film (Fig. 4.10), and from that calculate the scattering strength of an average TiO_2 particle (Fig. 4.5).

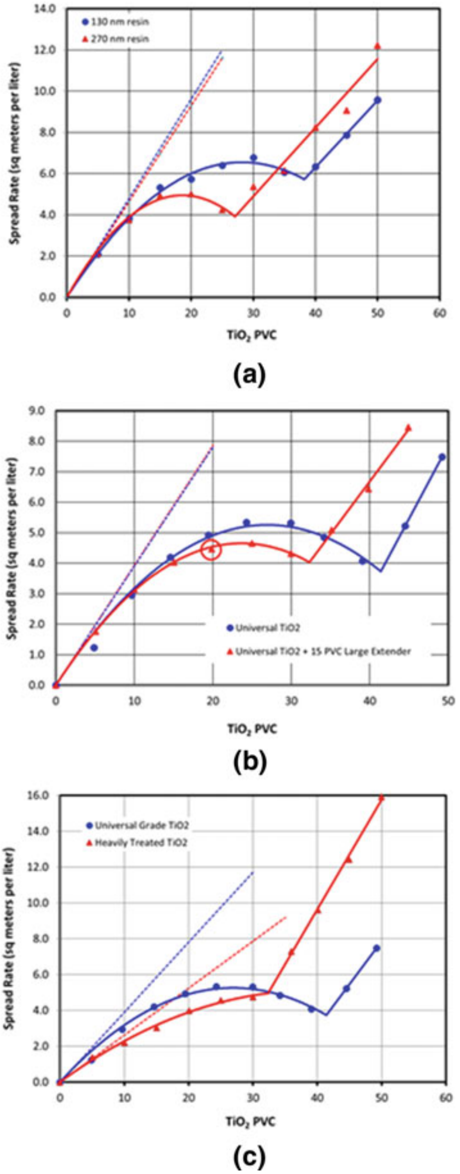


Fig. 4.10 Opacity versus PVC curves for the paint pairs shown in Fig. 4.6. Dotted lines show expected scattering in the absence of scattering volume overlap (i.e., they are curve tangents at the origin). **a** Universal TiO_2 pigment incorporated into paints with two different sizes of resins. **b** A universal TiO_2 pigment alone and with 15 PVC large extender. **c** Two different grades of TiO_2 pigment in the same paint as shown in (**b**)

would ever be formulated with such a high TiO_2 content! Instead, when a high PVC is desired, high levels of extenders are used. It is important to note that the opacity losses seen here are unavoidable since they are due to the fundamental physics behind dependent light scattering, rather than to poor paint formulation.

The Effective TiO_2 PVC

In paints containing only TiO_2 and resin, the PVC tells us not only how many TiO_2 particles are present in the film, but also the extent of TiO_2 crowding. As was shown in Chap. 3, Fig. 3.12, and reproduced here as Fig. 4.11, we can use simple geometry to calculate the surface-to-surface distances of ideally spaced 0.25 micron TiO_2 particles as a function of PVC. In paints that contain extender particles, however, the relationship between TiO_2 PVC and pigment crowding is altered. In particular, in the presence of extender particles, the TiO_2 particles are typically crowded more closely together than Fig. 4.11 would indicate.

When extender particles are present, it is useful to separate the information that the PVC tells us about the number of TiO_2 particles present in the paint from the information that it tells us about the degree to which these particles are crowded. We use TiO_2 PVC, as calculated in Eq. 4.2, to characterize the number of TiO_2 particles present in the film. To characterize the degree of TiO_2 crowding in the paint containing extender, we will develop a method to calculate the PVC value that reflects the same degree of TiO_2 crowding in the paint without extender. That is, we will characterize the degree of TiO_2 crowding in a paint containing extender, and with a certain TiO_2 PVC that we will call X, by saying it is the same as the degree TiO_2 crowding in a paint made without extender at a TiO_2 PVC of Y. This will be further clarified below.

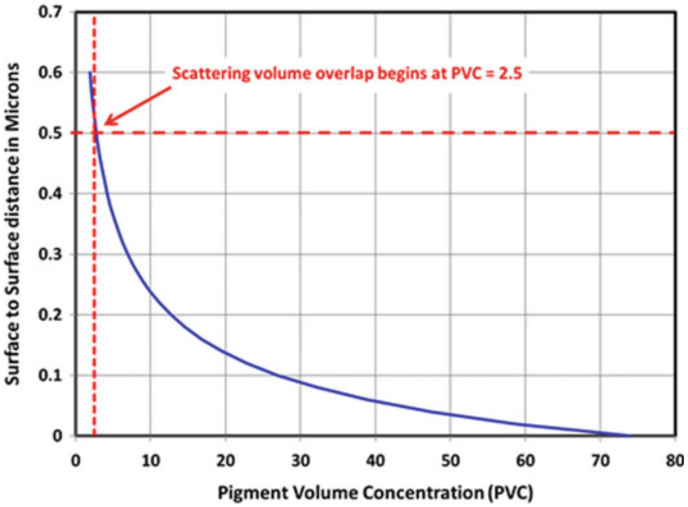


Fig. 4.11 Surface-to-surface distances for perfectly spaced 0.25 micron particles as a function of particle concentration [6]

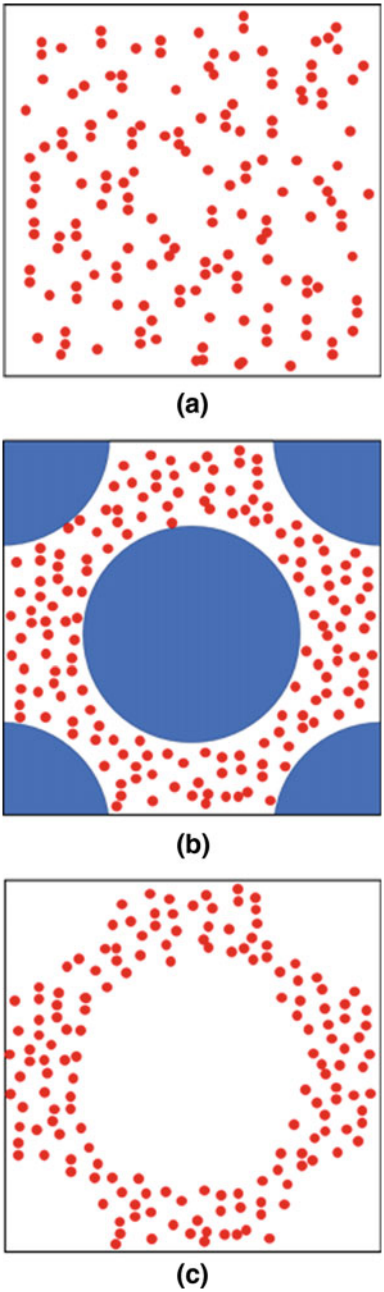


Fig. 4.12 Crowding of TiO_2 particles (red) by the presence of large extender particles (blue). All three fields have the same number of TiO_2 particles

The Effect of Large Extender Particles on TiO_2 Crowding

If we compare paints made with the same concentration of TiO_2 particles, one paint with large extender particles and the other without, we find that the degree of TiO_2 crowding is much greater in the paint made with large extender. The direct cause of this is that the TiO_2 particles cannot occupy the same regions in the film that are already occupied by the large extender particles. Instead, the TiO_2 particles must crowd into the interstitial voids between the extender particles. From a TiO_2 packing viewpoint, we can ignore the volume of film occupied by the extender particles when determining the extent of TiO_2 crowding.

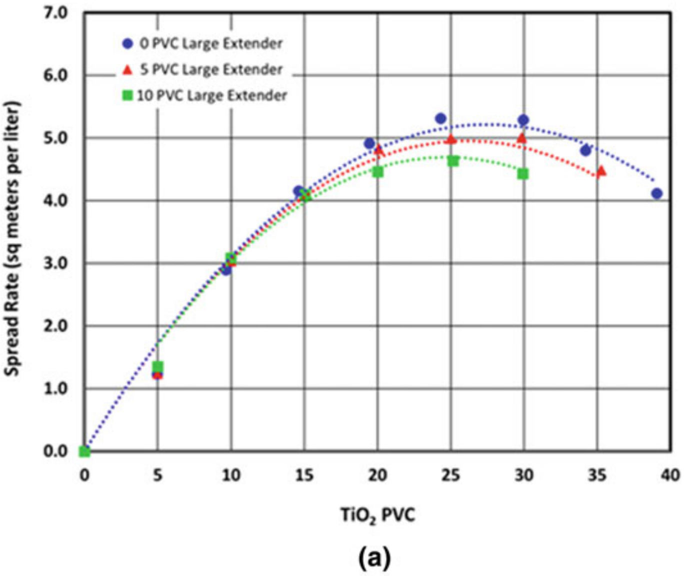
This crowding is illustrated schematically in Fig. 4.12. In Fig. 4.12a, we see a paint for which TiO_2 is the only particle. As is apparent in this figure, the randomly positioned TiO_2 particles are entirely spread out within the entire region, and the scattering volumes of the particles overlap one another to only a minor extent. The situation is quite different when large extender particles are present (Fig. 4.12b). Here, despite the film having the same total volume and the same number of TiO_2 particles, the distribution of the TiO_2 particles is much different. This is more easily seen in Fig. 4.12c, where the TiO_2 particles are located in the same positions as in Fig. 4.12b, but the large extender particles have been removed for clarity. We see that the TiO_2 particles are much more crowded in the presence of large extender particles than in their absence.

Clearly the relevant volume for calculating the extent of TiO_2 crowding is not the entire volume of the paint film, but rather the volume available for TiO_2 particle occupation. Stieg noted that when the extender particles are of the same size as the TiO_2 particles or smaller, they do not restrict the volume available for TiO_2 particle occupation in the same way as large extender particles [8, 9]. He proposed that the volume used to calculate the TiO_2 PVC when we are interested in characterizing particle crowding is simply the entire volume less than the volume of the large extender particles. Stieg referred to the PVC value calculated in this way as the "effective PVC" of the pigment. His calculation for effective PVC is given in Eq. 4.9.

$$Effective\, TiO_2\, PVC = \frac{TiO_2\, volume}{(small\, extender\, volume) + (TiO_2\, volume) + (resin\, volume)} \tag{4.9}$$

The success of Stieg's effective TiO_2 PVC concept for paints containing relatively low concentrations of large extenders can be seen in Fig. 4.13. In Fig. 4.13a, the spread rates of paints are plotted as a function of the TiO_2 PVC as calculated by Eq. 4.2. Here we see the negative effect that the large particles have on TiO_2 crowding, as evidenced by the drop in spread rate with increasing extender content at a given TiO_2 PVC. We see that this drop is minimal at low TiO_2 concentrations, as expected, since even in the presence of the large extender particles there is plenty of room available for the TiO_2 particles to remain well separated at these low TiO_2 PVC values.

Using Stieg's effective PVC concept, we can make a model of expected opacity as a function of both extender PVC and TiO_2 PVC. The results from this model are plotted as dashed lines in Fig. 4.13a. Note that these are not best fit lines for the data



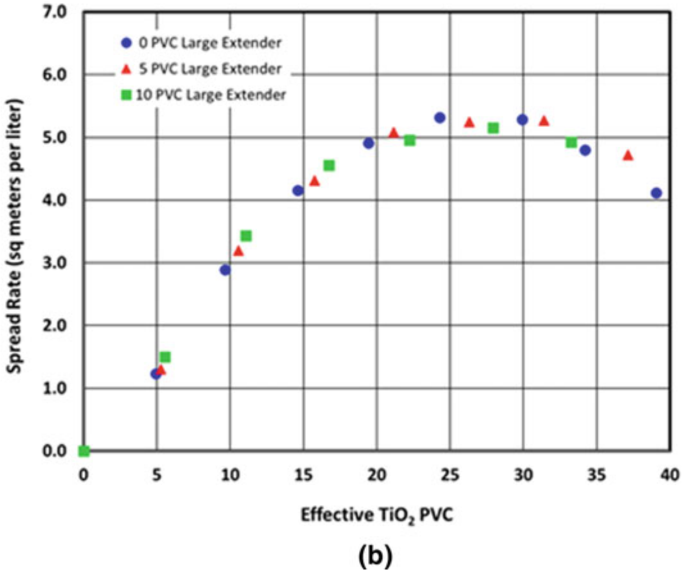


Fig. 4.13 Response of spread rate to TiO_2 concentration in paints containing large extender particles. **a** Based on actual TiO_2 PVC. The dashed curves are from the effective PVC model, not best fit lines to the data. **b** Based on effective TiO_2 PVC

points on the graph, but rather are the values predicted by the model. The details regarding model construction are given in the appendix.

An alternative way to demonstrate the effective PVC concept is to multiply the spread rate of a paint by the ratio of the effective TiO_2 PVC over the actual TiO_2 PVC and plot the result against the effective TiO_2 PVC (rather than the actual PVC, as shown in Fig. 4.13a), as shown for this dataset in Fig. 4.13b. When this is done, the data points for the different paint systems will fall on a common curve if the assumptions associated with the effective PVC value are valid.

In Fig. 4.13, the concentrations of large extender are relatively modest (only as high as 10 PVC). At higher extender concentrations, the effective TiO_2 PVC concept fails to model the opacity data accurately. This can be seen in Fig. 4.14. Here we apply the same process used to make Fig. 4.13b to the spread rates for paints made at higher concentrations of large extender. In this case, the results do not agree with those predicted by the effective PVC model. The failure of the effective PVC model at high concentrations of large extender particles is due to the resin demand of these particles. The resin required to fulfil the resin demand of the large extender particles decreases the amount of resin available to separate the TiO_2 particles, and so the TiO_2 particles are closer together than the effective PVC model calculates. This same effect on TiO_2 scattering efficiency can also be seen for small extender particles, as will be discussed in detail in the following section.

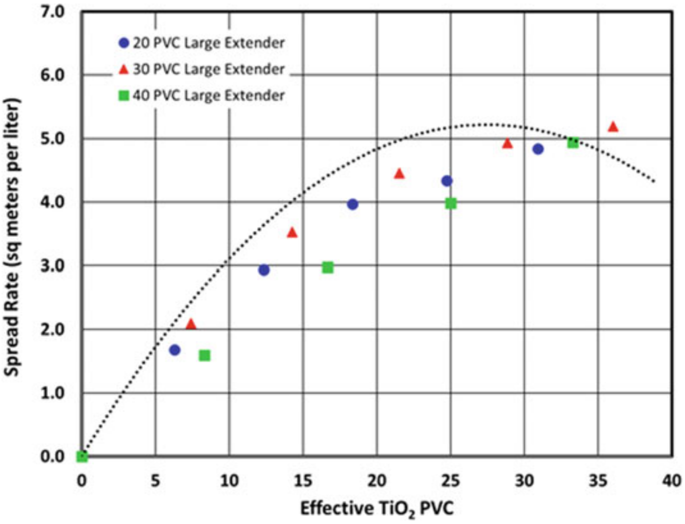


Fig. 4.14 Effective PVC concept at high large extender concentrations. The dotted black line is the best fit line for the three series shown in Fig. 4.13b

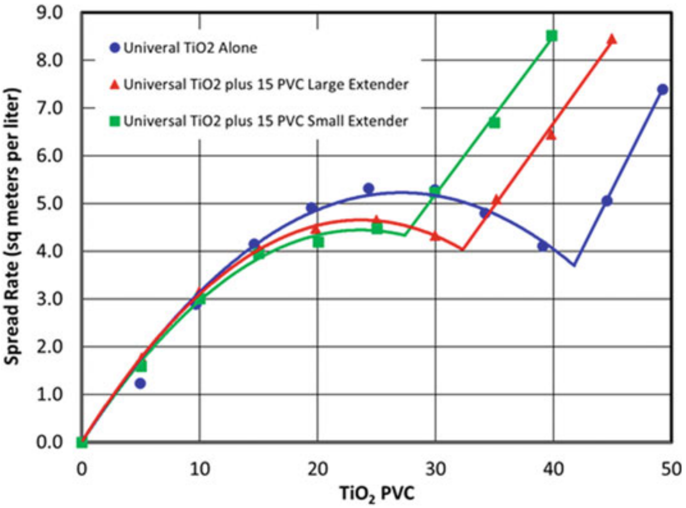


Fig. 4.15 Effect of large and small size extender particles on paint opacity

The Effect of Small Extender Particles on TiO_2 Crowding

Because well-dispersed small extender particles do not create the same large, contiguous regions of inaccessibility to TiO_2 pigment particles that an equal volume of large extender particles create, we might assume that the replacement of resin by small extender particles would not affect TiO_2 particle spacing. However, experiments show that while this assumption is often correct, it is sometimes incorrect. In fact, the presence of small extender particles can, in some cases, negatively affect paint opacity by roughly the same extent as an equal volume of large extender particles [10]. This is shown in Fig. 4.15, which compares the opacity versus PVC curves for paints made with a universal grade of TiO_2 alone and mixed with either a 15 micron extender or a 0.8 micron extender.[14]

A different mechanism applies to the reduction in TiO_2 scattering strength in the presence of small extender particles than that applied to large extender particles. This mechanism is related to that which explained the failure of the effective PVC concept at high concentrations of large extender particles, discussed earlier (Fig. 4.14). Both mechanisms are based on the resin demand of the extender particles.

Resin demand was discussed in Chap. 2 and is defined as the amount of resin required to bring a collection of particles to their CPVC point, that is, the amount of resin required to give each particle a thin (monomolecular) coating and to fill the spaces between the particles when they are packed at their highest density. This can also be described as the amount of resin that absorbs into the particle bed and is

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[14] It is important to repeat that the laboratory paints used in these experiments were not formulated to be commercially viable, but rather to demonstrate certain principles. As such, in some cases, their behaviors cannot be directly extrapolated to those of commercial paints.

often measured using the oil absorption test, as discussed below in the section on measuring the CPVC.

To understand the role of extender resin demand in TiO_2 particle spacing, we will return to our analysis of the increase in TiO_2 particle crowding when large particles are introduced into the paint film (see Fig. 4.12), and the opacity loss due to this crowding. In the previous section, we approached this opacity loss from a geometric viewpoint. The physical volume of the film occupied by the extender particles is unavailable to the TiO_2 particles, and so the TiO_2 particles crowd together into the regions that are available to them (the interstitial voids between the large particles). The degree of crowding was quantified by calculating the effective TiO_2 PVC, which omits the large particle volume from the PVC calculation.

There is an alternative interpretation of the crowding effect. This interpretation focuses on the resin, rather than the extender particles. To understand this approach, we must first consider the different roles that resin plays in a paint film [6].

We begin by examining a film that is at the CPVC of the paint system. Here the particles are packed at their densest configuration. A portion of the resin coats the particles, and the remainder fills the voids between them. The combined amounts of resin are the resin demand of that particle mix. Paints formulated below their CPVC have a higher resin concentration than at the CPVC, and the resin in excess of the resin demand is situated between the particles, pushing them apart and decreasing their crowding (this is often referred to as diluting the particles). This resin improves the scattering efficiency of the individual TiO_2 particles.

For the sake of clarity, we will refer to the resin that coats the particles as "type 1" resin, which fills the voids between the particles at their densest packing as "type 2" resin, and the remaining resin, which pushes the particles apart from their densest packing, as "type 3" resin.[15] These designations are based on the role of the resin alone—the different types of resin are chemically and physically identical.

The amounts of types 1 and 2 resin determine the CPVC of the paint system[16] while the amount of type 3 resin determines the actual PVC—the greater the amount of type 3 resin, the greater the spacing between the particles and so the lower the PVC. Classifying the resin into these three types is also useful in explaining one reason for the CPVC of small particles to be lower than for large particles (Fig. 4.2). Because the surface areas of small particles are greater, on an equal volume basis, than large particles, their type 1 resin requirements are also greater. This increases the amount of resin at the CPVC conditions of the small particles (that is, their resin demand), and so decreases their CPVC value.

Returning to our alternative interpretation of the crowding effect, we next consider the addition of large extender particles to paints formulated with only TiO_2 and resin that are at a PVC value below the CPVC. Recall that we cannot simply "add" extender particles to this film—instead we substitute some of the resin with an equal volume of large particles. The resin that is substituted is not a random mix of the three types of

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[15] Type 3 resin is often referred to a "free" resin, as it is not bound to the role of satisfying the resin demand of the particle mix.

[16] That is, the sum of the amounts of types 1 and 2 resin is the resin demand of the particles.

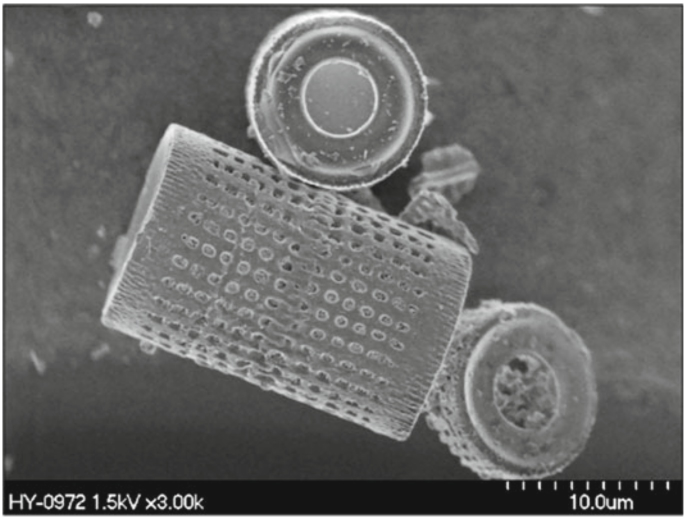

Fig. 4.16 Example of diatomaceous earth particles [6]

resin—it is exclusively type 3 resin.[17] We are therefore replacing resin that separates TiO_2 particles with an equal amount of a material that is too large to get in between individual TiO_2 particles in the same way that type 3 resin can. From this viewpoint, the increase in TiO_2 particle crowding when large extender particles are formulated into a paint is due to a loss of type 3 resin.

If we extend this logic to the small particles, we would conclude that they should not cause a loss in opacity like their large counterparts because the small particles should be able to occupy voids between the TiO_2 particles and separate them in the same way that the type 3 resin they are replacing does. This is, in fact, an implicit assumption in the effective PVC model.

However, as seen in Fig. 4.15, this is not the case—the opacity for paints made with small extender (squares) is lower than for paints made in the absence of extender (circles). This analysis omits the fact that small particles reduce the amount of type 3 resin available in the paint system due to their resin demand [8]. That is, replacing a given volume of resin with small extender particles removes that volume of type 3 resin and converts some of the remaining type 3 resin into the types 1 and 2 resin needed to satisfy the small extender particles.

This effect can be illustrated by considering diatomaceous earth. This is a unique extender particle that is composed of large particles that are very porous (Chap. 9). These fascinating particles are the fossilized remains of tiny, one-celled organisms that encapsulate themselves in a porous shell (Fig. 4.16). These particles are in the size range of the large extender particles used in the paints discussed in this chapter, but they have a much higher resin demand because resin is needed not only to coat

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[17] Above the CPVC, type 2 resin is exchanged. In the case of extremely high PVC values, when the reservoir of type 2 resin is depleted, then type 1 resin is exchanged.

the particles and fill the interstices between them, but also to fill the pores and open spaces within them.

As a result of their higher resin demand, the deleterious effect of diatomaceous earth on paint opacity is much more severe than the effect that extender particles of equal size (10 to 12 microns) have on opacity—in fact, the loss of opacity at equal PVC for diatomaceous earth is roughly double that of the large extender particles.[18] We can understand this readily—first, each particle of diatomaceous earth occupies the same volume as do large extender particles. Second, because their void fraction is so high (approximately 85%), a roughly equal volume of resin is required to fill the intraparticle voids. Thus, roughly twice the amount of type 3 resin is lost for diatomaceous earth as for solid extender on an equal particle volume basis.

We can now understand why the effective PVC concept fails at high concentrations of large extender particles. The effective CPVC calculation (Eq. 4.9) takes into account the amount of type 3 resin replaced based on the volume of the extender particles but does not include the type 3 resin loss due to the resin demand of the large particles, that is, the amount of type 3 resin that must convert to the type 1 resin that adsorbs onto the extender particles. Large particles consume relatively little type 1 resin, and so the error from omitting this source of type 3 resin loss from our effective PVC calculation is minor at low extender concentrations. However, at higher concentrations of large extender particles, the amount of type 3 resin lost due to conversion to type 1 resin is enough to negatively impact paint opacity (Fig. 4.15).

The fact that the opacity loss due to small particles is roughly equal to that of large particles in our laboratory paints can be understood by considering that the effective PVC calculation should include the volume of lost type 3 resin in the same way that it includes the volume of large extender particles. Equation 4.10 is the traditional way of calculating TiO_2 PVC (this is the same equation that was listed as Eq. 4.1 earlier in this chapter and is repeated here for convenience). To measure the effective PVC based on the volume of large extender particles, we modified the denominator of this equation by subtracting (removing) the volume of large particle extender (Eq. 4.11a). This equation simplifies to the effective PVC equation given earlier as Eq. 4.9 and repeated here as Eq. 4.11b.

$$\mathrm{TiO_2\,PVC} = \frac{\mathrm{TiO_2\,volume}}{(\mathrm{extender\,volume}) + (\mathrm{TiO_2\,volume}) + (\mathrm{resin\,volume})} \tag{4.10}$$

$$\mathrm{Effect\ TiO_2\ PVC} = \frac{\mathrm{TiO_2\ volume}}{\left[(\mathrm{TiO_2\ vol}) + (\mathrm{resin\ vol}) + (\mathrm{large\ extender\ vol})\right] - (\mathrm{large\ extender\ vol})} \tag{4.11a}$$

$$\mathrm{Effective\,TiO_2\,PVC} = \frac{\mathrm{TiO_2\,volume}}{[(\mathrm{TiO_2\,volume}) + (\mathrm{resin\,volume})]} \tag{4.11b}$$

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[18] This is true when comparing paints below the CPVC value. Small amounts of diatomaceous earth can increase paint opacity by decreasing the CPVC to a level below the paint PVC. The air voids created by the CPVC dropping below the PVC will scatter light, as discussed elsewhere in this chapter and in Chap. 3.

For paints made with small extender particles, we can take into account the available volume loss due to the resin demand of these particles by subtracting their resin demand from the denominator of the TiO_2 PVC equation in a similar way that we subtracted the large extender particle volume from the denominator. This is done in Eq. 4.12a.

$$\text{Effect}\,TiO_2\text{PVC} = \frac{TiO_2\,\text{volume}}{[(TiO_2\,\text{vol}) + (\text{resin vol}) + (\text{small extender vol})] - (\text{resin demand vol})} \tag{4.12a}$$

$$\text{Effective}\,TiO_2\,\text{PVC} = \frac{TiO_2\,\text{volume}}{[(TiO_2\,\text{volume}) + (\text{resin volume})]} \tag{4.12b}$$

We can estimate the resin demand of most small extender particles as roughly the same volume as the particles themselves (this implies a CPVC value for the small extender particles of 50, which is consistent with those measured for most small particles). If the small extender volume and the resin demand volume for the small extender are equal, then we can simplify Eq. 4.12a to give Eq. 4.12b, which is exactly the same as the standard effective TiO_2 PVC equation when large extender particles are present (Eq. 4.11a). We can therefore understand how, in some paints, the effect of extender PVC on TiO_2 crowding is the same for small extender particles as large ones, as is borne out in Fig. 4.15.

The physical implications of this mathematical analysis are displayed schematically in Fig. 4.17. Here we consider, in two dimensions, the ideal spacing of the same number of small particles (TiO_2) in four particle scenarios.[19] The TiO_2 particles (0.25 micron diameter) are at the same concentration (20 PVC)[20] in all four scenarios. The first scenario (Fig. 4.17a) has TiO_2 as the only particle present, and the surface-to-surface distance between nearest neighbors (of which there are six) is 0.283 microns.

In the second scenario, a large hexagonal extender particle (side length 2.57 microns) is placed in the center of the field (Fig. 4.17b). This represents an extender PVC of 25. Again, the TiO_2 particles are positioned such that they pack as tightly as possible in the space available to them. Using Eq. 4.11b, we calculate the effective PVC of the TiO_2 to be 26.67. In this scenario, the surface-to-surface distance between nearest TiO_2 neighbors (of which there are again six) is only 0.212 microns, demonstrating the crowding effect of large extender particles.

The third scenario is somewhat more complex. Here we have replaced the large extender particle with small extender particles having the same total volume.[21] This collection of particles is packed together as tightly as possible, that is, at their CPVC

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[19] A similar analysis applies to three dimensions, but this is more difficult to illustrate in figures.

[20] Note that we will refer to the concentration of the two-dimensional particles as if based on volume (PVC) although, technically, since this is a two-dimensional analysis, the concentration should be expressed on an area basis.

[21] The number of small extender particles is such that the volume of each is 25% greater than that of a TiO_2 particle. In this way, there are the same number of small extender particles in the film (their concentration is 25 PVC) as are TiO_2 particles (their concentration is 20 PVC).

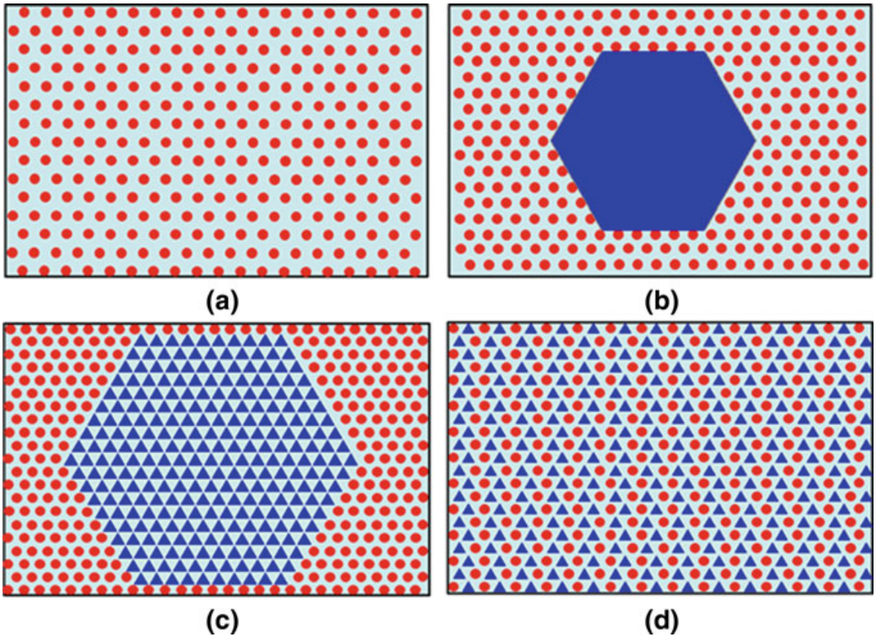

Fig. 4.17 Particle spacing for different combinations of TiO_2 (red) and extender (blue) particles in a field of resin (gray). **a** TiO_2 particles (20 PVC) only. **b** TiO_2 particles (20 PVC) and large extender particle (25 PVC). **c** TiO_2 particles (20 PVC) and small extender particles (25 PVC) at their tightest packing (CPVC = 50). **d** TiO_2 particles (20 PVC) and small extender particles (25 PVC) distributed throughout the film

value, which we will define here as 50. The small particles occupy twice the space as the single large particle because of this and result in the removal of 25 PVC resin (the resin demand for 25 PVC of small particles). For the purposes of calculating the effective PVC of the TiO_2 particles, we use Eq. 4.11b and treat the collection of small particles, with their attendant resin, as a single large particle with twice the size of the large extender particle. Alternatively, we can use Eq. 4.11b, with the amount of small particle extender and excluded resin volume being equal (25 PVC each). In either case, we calculate an effective TiO_2 PVC of 40. The additional crowding due to the increase in inaccessible area between scenarios B and C leads to a reduction in the TiO_2 surface-to-surface distance to 0.127 microns.

Were we to terminate our analysis here, we would conclude that the crowding of the TiO_2 particles in the case of small extender particles (Fig. 4.17c) is twice that of an equal volume of large particles (Fig. 4.17b). We know, however, that this is not the case, as shown in Fig. 4.15. What is missing from the analysis is that there are two contributors to TiO_2 crowding in the case of the small particles (Fig. 4.17c). The first, as drawn in this image, is crowding due to the volume of the small particles being inaccessible to the TiO_2 particles (as is the case for the large particle in Fig. 4.17b). The second contributor is that the small particles have made an equal volume of type

Table 4.1 Analysis of the four scenarios described in Fig. 4.17

Scenario[a]	TiO_2 PVC	Effective TiO_2 PVC	Extender PVC	Surface-to-surface distance (μ)	Number of near neighbors
A	20	20	0	0.283	6
B	20	26.7[b]	25	0.212	6
C	20	40.0[c]	50[d]	0.127	6
D	20	40.0[c]	50[d]	0.127	2

[a] See Fig. 4.17 and the text for the description of each scenario

[b] Calculated using Eq. 4.9

[c] Calculated based on the resin available to the TiO_2 (see Eq. 4.12b)

[d] This includes the resin demand volume for the small extender particles

3 resin inaccessible to the TiO_2 particles (the resin demand of the small extender). The contribution to crowding for both of these components is, in this case, equal.

Figure 4.17c is quite artificial since it is a near impossibility that a random mix of the TiO_2 and small extender particles would result in all of the small extender particles positioning together as one mass. Instead, we would expect these particles to be interspersed with the TiO_2 particles. This is shown in Fig. 4.17d. In this case, the penalty due to exclusion of the TiO_2 particles from region occupied by the small particles is removed, but the penalty due to the resin demand of the small particles remains.

In this arrangement, the surface-to-surface distance between each TiO_2 particle and its nearest neighbors remains at 0.127 microns. However, the number of near neighbors has decreased from six (Fig. 4.17c) to two (Fig. 4.17d). This reduces the amount of scattering volume overlap. Based on the similarity in the measured scattering power of paints made with large and small extender particles (Fig. 4.15), we conclude that the total extent of scattering volume overlap must be roughly the same for large and small extender particles at equal extender concentrations.

The numerical details of this analysis are given in Table 4.1.

Using the Opacity Versus PVC Curve to Measure the Effective TiO_2 PVC

The red line in Fig. 4.8 is a special case of a more general family of lines that we can place on the opacity versus PVC chart. This family comprises all lines that pass through the origin. The significance of these lines is that the scattering efficiencies of the individual TiO_2 particles for all paints that fall on the same line will be the same.

We can understand this by recalling that the scattering efficiency of an average particle in a paint is the scattering strength of the paint divided by the number of particles in it. In the opacity versus PVC curve, the y-axis value is the scattering strength of the film and the x-axis value is the number of particles, measured as the particle concentration. Any point on a straight line through the origin will have the same ratio of the two and therefore the same average scattering efficiency per individual TiO_2 particle.

We can use lines through the origin to experimentally determine the effective TiO_2 PVC of a given paint. Recall that the importance of the effective TiO_2 PVC concept is that it describes the local concentration of TiO_2 particles in a paint, omitting the regions of the film that are inaccessible to the TiO_2 particles (such as the regions occupied by individual large extender particles). As stated earlier, the scattering ability of a TiO_2 particle in a paint film is determined as if the concentration of TiO_2 particles was at their effective PVC value, rather than at their true PVC.

We will demonstrate how the lines of constant TiO_2 scattering efficiency can be used to determine the effective TiO_2 PVC using the paint made with 20 PVC TiO_2 and 15 PVC large extender (circled red triangle in Fig. 4.10b) and the series of paints made with the TiO_2 alone (blue line in Fig. 4.10b). We reproduce this information in Fig. 4.18. Because the large extender particles restrict the volume of film accessible to the pigment particles, the pigment particles scatter light less efficiently in the presence of extender than in its absence and so the red triangle in Fig. 4.18 is below the blue curve.

We can quantify the opacity cost of the extender by comparing the spread rate of the paint made in the absence of extender (4.93 m^2/l) to that in the presence of extender (4.47 m^2/l). This shows that the paint film loses roughly 10% of its scattering power by the exchange of 15 PVC resin with an equal volume of large extender.

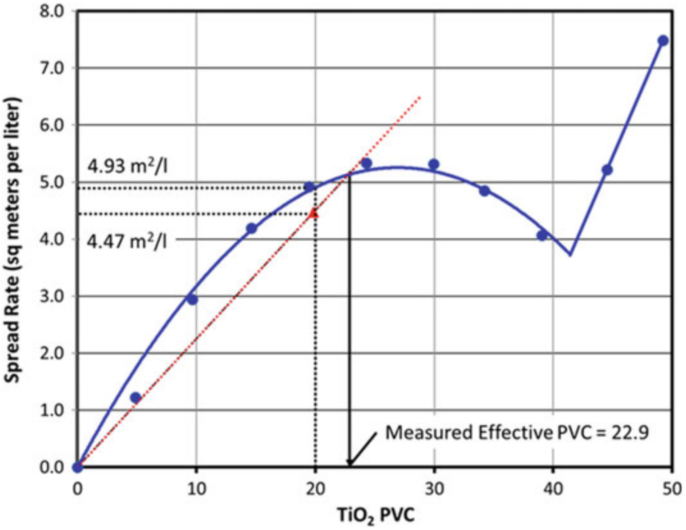

Fig. 4.18 Comparing a paint made with 15 PVC large extender and 20 PVC universal TiO_2 (red triangle) to a series of paints made with the same universal TiO_2 in the absence of extender (blue line)

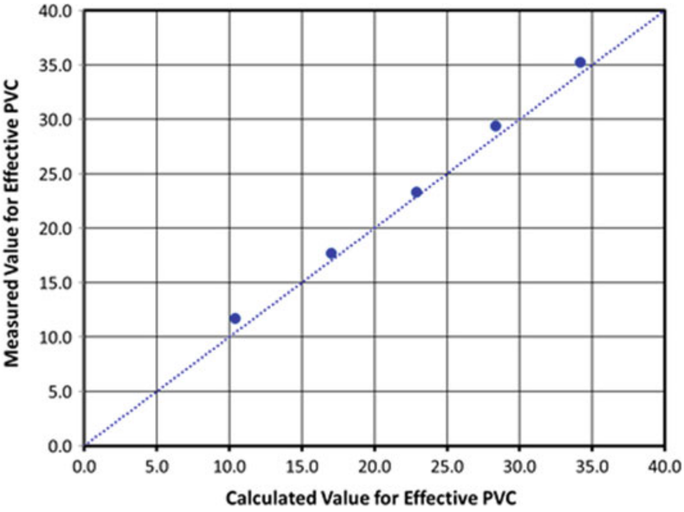

Fig. 4.19 Comparison of effective PVC for the red curve in Fig. 4.10-B as calculated by Eq. 4.6 to the value experimentally determined as described in the text. The dashed line represents perfect agreement between the methods rather than the best fit line

In Fig. 4.18, we extend a red dashed line from the origin through the extended paint to the curve for the non-extended paint. The red line and blue curve intercept at a TiO_2 PVC value of 22.9. Since the average scattering efficiencies of the individual TiO_2 particles for all paints that are on this line are the same, the TiO_2 particles in the extended paint scatter light as if they were at 22.9 PVC rather than at their actual concentration of 20 PVC. That is, the measured effective PVC for this paint is 22.9. This is in good agreement with the value calculated from Eq. 4.9 (23.5 PVC).

We can extend this analysis to all paints made with 15 PVC large extender (shown in red in Fig. 4.10b) to determine the experimental values for the effective PVC for this paint series. In Fig. 4.19, we compare the experimentally determined effective PVC values to the calculated values. As can be seen, the values are in excellent agreement. The measured values are slightly higher than the theoretical values, possibly because of the slight resin demand of the large extender particles (this factor is not captured in Eq. 4.9).

For the extended paint shown in Fig. 4.18, we calculated a loss of the average TiO_2 scattering strength, due to crowding by the large extender particles, of roughly 10%.[22] This value is not uncommon for extended paints. In fact, many paints have significantly greater levels of extender, and in these paints the loss in average particle scattering strength can be much larger. As a worst-case example, a paint was made similar to the extended paint in Fig. 4.18, except with 25 PVC TiO_2 and 25 PVC

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[22] Here we measure efficiency on the basis of the unextended paint, not on the basis of the scattering value of the TiO_2 pigment in the absence of scattering volume overlap (the basis for the analysis of Fig. 4.8).

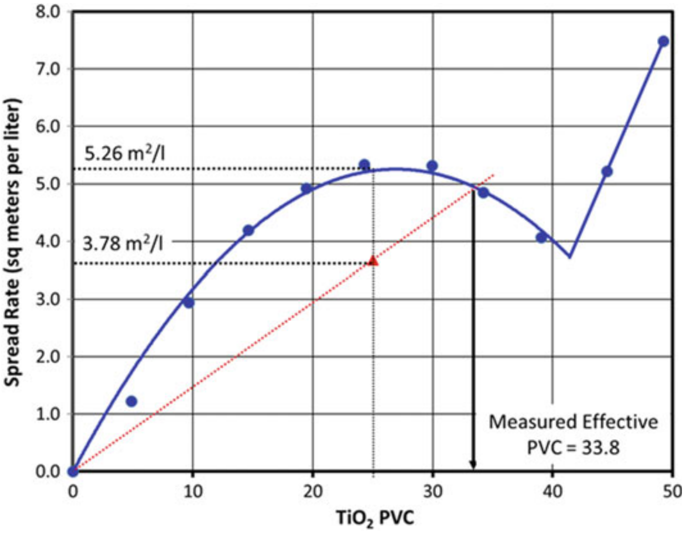

Fig. 4.20 Comparing the paint made with 25 PVC large calcium carbonate extender and 25 PVC TiO_2 (red triangle) to a series of paints made with the same universal TiO_2 in the absence of extender (blue line). The red dashed line indicates the TiO_2 scattering efficiency of this paint

extender.[23] This is shown in Fig. 4.20. Here the paint loses nearly 30% of its scattering value due to crowding of the TiO_2 pigment by the large extender particles. The measured effective TiO_2 PVC of this paint, 33.8, is in good agreement with the calculated value or 33.3.

Measuring the CPVC

The CPVC value for a specific single particle type or mixture of more than one particle types is typically measured in the laboratory using one of two strategies. In the first, paints are made over a range of PVC values while keeping the composition of the particle mix the same. This is most conveniently done by making master paints at the high and low ends of the PVC range of interest, then filling in paints at intermediate PVC values by mixing appropriate amounts of the two master paints.[24] Drawdowns are made of these paints and the paints tested for a property that shows a significant change at the CPVC.

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[23] We consider this a worse case sample because the TiO_2 PVC—25 in this case—is at the maximum in the curve for the unextended paint (i.e., the blue curve in Fig. 4.18 and elsewhere). No reasonable paint would be formulated at a TiO_2 PVC above the maximum of this curve.

[24] Note that the two master paints must be made at the same total solid volume concentration, so that equal thicknesses of wet paint films will give equal thicknesses of dry films.

The film properties that change at the CPVC can be grouped into the following categories [11]:

- *Opacity*—Any of the opacity tests outlined in Chap. 13 will show a significant increase at the CPVC.
- *Gloss*—Air entrained in a film will cause the surface of that film to roughen. Gloss values are sensitive to roughness of this magnitude and so decrease at the CPVC. That said, this is among the least precise techniques of determining the CPVC since gloss generally decreases with PVC below the CPVC. The change in the rate of gloss loss can be similar in the two concentration regimes (below and above the CPVC). In addition, some paints below the CPVC are formulated to have low gloss (e.g., eggshell and flat sheens), which further compounds the uncertainty inherent in this method.
- *Profilometry*—This is an alternative technique to measure surface roughness. It is generally more accurate than gloss loss but requires a special instrument. Overall, it is less preferred than many other methods.
- *Density*—Below the CPVC, the measured densities of dry films agree quite well with the those calculated based on the densities of the constituents (i.e., the mass weighted average density). Above the CPVC, the measured density is lower than the calculated density due to the presence of air voids. This is a fairly accurate means of determining the CPVC, and also has the advantage that the air content of the film (that is, its porosity) can be determined from the difference in measured and calculated densities.
- *Pore Volume*—Pore volume of the paint film can be measured directly using mercury porosimetry. Below the CPVC there are no pores, and so this value will be zero. Like density, this method provides volumetric information about the pores. In addition to the total volume of the pores, it also reports the volumes on a size basis. This method can also be used to determine the void volume of hollow sphere polymer particles, as they collapse at specific pressures (this pressure changes from one grade of hollow sphere polymer to another). A specialized instrument is required for this test.
- *Elasticity and Tensile Strength*—These related properties drop sharply at the CPVC point, making them promising options for CPVC determination. However, they require free-standing films (i.e., films separated from the substrate), which makes sample preparation difficult and time-consuming. In addition, these properties can also be affected by the degree to which the latex particles in a waterborne paint coalesce, and so factors such as coalescent levels, drying time, and drying temperature must be carefully controlled.
- *Scrub Resistance*—This is an alternative method of determining film strength. This test differs from elasticity and tensile strength as it does not require a free-standing film (in fact, a durable substrate is required). Paints are submerged in a soap solution and scrubbed with a mechanical device. Scrub resistance is quantified as either the film loss after a certain number of scrub cycles or the number of scrub cycles to a predetermined failure point. As with elasticity and tensile

strength, the results of this test are affected not only by the presence of air, but also by how well the resin particles coalesce during film formation.

- *Stain Resistance*—Capillary forces pull a liquid deep into a film that has interconnected pores, and the degree to which a liquid stain that is applied to a film surface and then wiped off will discolor that surface changes at the CPVC value. However, there is some variability in this measurement when different liquids are applied, especially if the liquid carriers are chemically different (and so have different surface tensions) for the different stain materials.
- *Corrosion Resistance*—The ability of a paint film to prevent corrosion of a reactive substrate will obviously decrease substantially when the film contains pores. This technique is seldom used, however, because it, too, is sensitive to the quality of resin particle coalescence and because of the relatively long exposure times (weeks) required.
- *Outdoor Durability*—Intrusion of rainwater or dew into a porous film will significantly decrease the durability of that film and its ability to protect the substrate from weather. However, this test is seldom used because these tests require months to years of exposure.
- *Electrical Conductivity*—Paints are drawn on a metal panel and allowed to dry in an oven overnight. They are then soaked in salt water for a period of time. The panels are removed from the saltwater bath and, while still wet, one electrode of a resistance meter is applied to the painted surface and another electrode to the back of the panel. The resistance will be low (conductance high) if there are pore channels that travel from the film surface to the substrate surface [12].

The second strategy for determining CPVC is to use oil absorption values (refer back to Chap. 2). In this procedure, oil absorption is measured for a well-mixed sample of the particle blend of interest [13]. The end point of the oil absorption test occurs when there is just enough oil to make a thin coating on all of the surfaces and to fill the gaps between the particles at their tightest packing. This is the same description as the CPVC, except that oil, rather than resin, is the diluting material in the oil absorption method. Under the assumptions of this equivalence, the CPVC can be calculated from oil absorption using Eq. 4.13.

$$\mathrm{CPVC} = \frac{100}{1 + \frac{(\mathrm{OA})(\rho)}{93.5}} \tag{4.13}$$

In this equation, the CPVC is given on a percent basis (0 to 100%), OA is the oil absorption value, and ρ is the density of the dry resin (in g/cc). The value 93.8 in this equation is one hundred times the density of linseed oil (the factor of 100 is included because oil absorption is reported as the grams of oil per 100 g of particles, and for Eq. 4.13 we use the grams of oil per gram of particles). Note that CPVC decreases as oil absorption increases, that is, there is a reciprocal relationship between them.

Although the oil absorption method generally predicts CPVC accurately for solventborne paints, it invariably over-estimates it for latex waterborne paints. The reason for this is that not all of the resin in the resin particles is free to flow into the crevices between the pigment and extender particles. Instead, resin particles can be considered as having two components—an outer component that can be solubilized by the coalescing agent and so can deform and flow, and an inner core that is shielded from the coalescing agent by the outer component and thus cannot deform or flow.[25] Since the resin in the core of the latex particles is unavailable for coating extender or pigment particles, or for filling the voids between them, more resin is required at the CPVC than for a solventborne paint (where all the resin is available for these roles). This results in a lower CPVC for a latex paint than for a solventborne paint, or than calculated using Eq. 4.13. This property of resin is referred to as its Binding Power Index (BPI) and will be discussed in detail in Chap. 10.

We will end this section with a note of caution. There are numerous examples in the literature of formulation experiments for which the oil absorptions values of particle mixtures (and the CPVC values calculated for them) are calculated by measuring the oil absorption values of the individual particle types and then using the weighted average of these values as the oil absorption for mixtures of them. While many mixture properties can be calculated as a weighted average of the properties of the individual particle types (e.g., density, composition, surface area, TGA weight loss, etc.), this is not the case for oil absorption or CPVC. As was clearly shown in Fig. 4.2 and discussed in the section on particle packing, the packing of particle mixtures can be very different than the packing of the individual constituents. For this reason, both oil absorption and CPVC must be measured for each particle mix and not inferred from the values for the individual mixture components.

Opacity Above the CPVC

Inclusion of air voids in the dry paint film increases light scattering by two mechanisms. First, as noted above, air voids scatter light. An extreme example of light scattering by air voids is the bright white color of unpigmented polystyrene foams (e.g., Styrofoam®). These materials generally contain no TiO_2 or other light scattering particles. Instead, they achieve complete opacity exclusively through air void scattering (on a volume basis these materials are 98% air).

The second mechanism by which air voids increase light scattering arises from the refractive index of air (1.0) being significantly less than that of the resin (1.5), extender (1.5), and titanium dioxide pigment particles (2.73). Air inclusion therefore lowers the average refractive index of the film and so increases the difference in refractive indices between the TiO_2 particles and their surroundings [14]. As such, air voids increase the scattering strength of the titanium dioxide pigment.

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[25] These two components of a resin particle should not be confused with the three types of resin described earlier. Resin type describes the role that a particular portion of resin plays in a paint film while the two components describe differences in the resin particle, rather than the paint film.

Dry Hide

The contribution of air voids to the opacity of a dry paint film is referred to as dry hide. This designation is derived from the fact that this opacity is only apparent in the dry paint but is completely missing in the wet paint. This is because the wet paint does not contain air voids—these are only created when the liquid carrier of the paint (typically water) leaves the film. Aspects of wet hide will be discussed later, but first we will consider the nature of dry hide.

The Opacity Versus CPVC Curve Above the CPVC

Referring back to Fig. 4.8, we see that the shape of the opacity versus PVC curve above the CPVC is quite different from that below the CPVC. More specifically, above the CPVC the opacity increases linearly with increasing PVC, while below the CPVC there is a decrease in the rate of increase in opacity as PVC increases, eventually leading to a net loss in film scattering power above a certain PVC value (for example, a PVC value of 27.1 for the paint system in Fig. 4.8).

As outlined above, the increase in film opacity with increasing PVC above the CPVC can be attributed to several factors. First, increasing the PVC increases the air void content of the film (see Fig. 4.9b). This provides the two benefits to light scattering and film opacity described above (the air voids scatter light themselves and they decrease the average refractive index of the region surrounding the TiO_2 particles).

As mentioned earlier, as the PVC is increased in paints above the CPVC, TiO_2 particle crowding does not increase. This is very different than increasing the PVC in paints below the CPVC, where an increase in PVC results in an increase in particle crowding. By definition, the particles cannot crowd any closer together than at the CPVC, and so when increasing the PVC in paints above their CPVC, we do not increase crowding or scattering volume overlap (instead we increase the number of particles by increasing film thickness).

Therefore, above the CPVC, increasing the PVC has the benefit of linearly increasing the number of light scattering centers (both TiO_2 particles and air voids) without the penalty of increasing the scattering volume overlap between the TiO_2 particles. As a result, we expect that paint opacity should also increase linearly. Figure 4.10 confirms this for a variety of paint systems.

Porosity Index

When characterizing paints according to their PVC value (and their CPVC value), our focus is on the particles within the film. While this is an important determinant of many film properties, it is often useful to characterize films that are formulated above the CPVC from an alternative viewpoint—that of the air voids. This is because the concentration of air voids affects many important properties of the film. These include opacity, as discussed elsewhere, as well as film integrity, stain resistance, and substrate protection.

The most obvious way to characterize the pore content of a paint film would be to do so by volume based on the entire volume of the film (Eq. 4.14), in a manner analogous to using the packing factor calculation (Eq. 4.5) to characterize particle volume. This quantity is termed the film porosity.

$$\text{Film Porosity} = \frac{\text{air volume}}{(\text{combined particle volumes}) + (\text{resin volume}) + (\text{air volume})} \tag{4.14}$$

Film porosity compares the volume of air to the combined volumes of all film components. In doing so, we are differentiating between air, on the one hand, and the solid components (resin and particles), on the other. While this differentiation is useful in some situations, particularly with regard to understanding the contribution of air to light scattering, it is not the only way we can quantify the air content of the film. An alternative is to quantify the air void volume by the porosity index, which is based only on the volumes of the air voids and the resin (Eqs. 4.15 and 4.16):

$$\text{PI} = \frac{\text{air volume}}{\text{air volume} + \text{resin volume}} \tag{4.15}$$

$$= 1 - \frac{\text{CPVC}(100 - \text{PVC})}{\text{PVC}(100 - \text{CPVC})} \tag{4.16}$$

The usefulness of the porosity index is that it combines air and resin into a single component. That is, we can consider the film to be composed of solid particles that are held together by an air/polymer mixture. We are quite accustomed to mixtures of air and polymer in our daily lives—these are simply solid foams. The porosity index tells us how much air is in this foam mixture, and as such it is an excellent indicator of many important film properties, as listed above. As a general rule, paints made with the same resin particles and having the same porosity index have the same degree of "foaminess" and so similar mechanical and stain properties.[26]

Specialized TiO_2 Grades for Paints Formulated Above the CPVC

TiO_2 spacing is of importance in all paints, especially in those formulated above the CPVC. Because of this, some TiO_2 grades have been specifically developed for high

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[26] This is true only to a first approximation for scrub resistance. Pore size can also affect scrub resistance, as will be shown in Chap. 16.

PVC systems. We introduced these grades earlier as “highly treated TiO_2”, a name that highlights their composition. We can also describe these same pigments as “high PVC grades”, as they are used only in paints near or above their CPVC.

As will be discussed in Chap. 7, the particles in these grades are encased in a thick layer of alumina and silica. These two oxides are present in the form of a highly porous aluminosilicate. Because it is porous, the aluminosilicate occupies a high volume when compared to its weight. This is important because a denser material would unnecessarily decrease the TiO_2 content of the pigment (and with it, the number of scattering centers per unit weight of pigment).

These materials have long been thought to consist of individual TiO_2 particles that are enveloped in a thick layer of porous aluminosilicates (Fig. 4.21a). This layer would prevent the TiO_2 cores of the pigment particles from touching one another and so restrict the loss of opacity in crowded paint systems. However, there is an alternative morphology that explains the spacing benefit of the aluminosilicates. These particles could be composed of agglomerates of a few TiO_2 particles held at a fixed distance from one another (Fig. 4.21b). This is consistent with electron micrographs of these particles (Fig. 4.22) and also with the shape of the opacity versus PVC curves for these materials below the CPVC (discussed below).

Before comparing the shapes of the opacity versus PVC curves for the two types of TiO_2 pigment, we will first consider the particle spacing implications for the two different morphologies. If this pigment exists as individual particles with thick

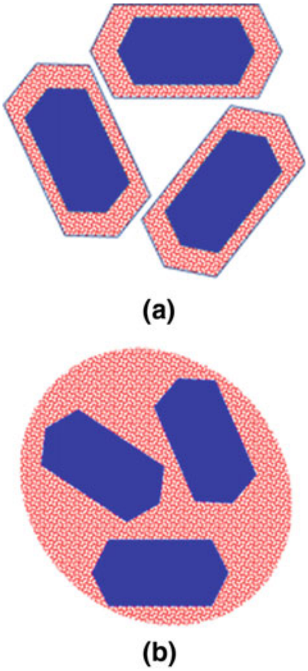

Fig. 4.21 Different particle morphologies for highly treated TiO_2. Blue shapes are TiO_2, red regions are aluminosilicate. **a** Individually coated particles. **b** Small agglomerates

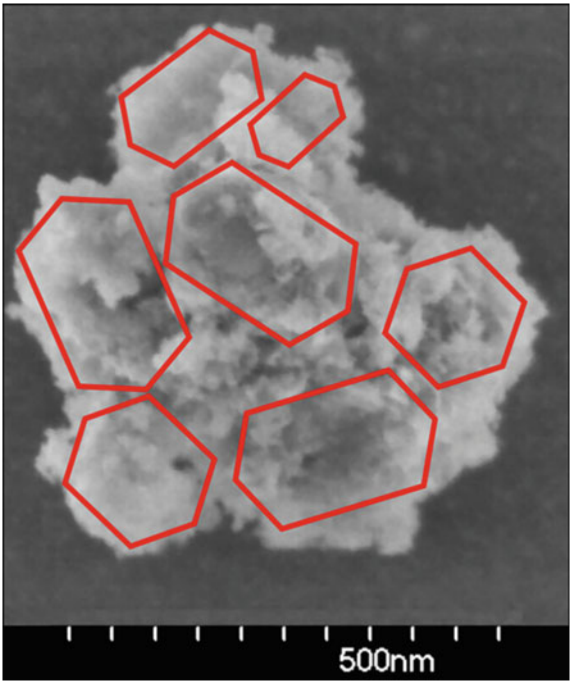

Fig. 4.22 Electron micrograph of highly treated TiO_2 pigment. Red lines indicate the rough shapes of the TiO_2 particles within the aluminosilicate agglomerate

coatings (Fig. 4.21a), then the particle spacing will change as the PVC changes, just as it does for the universal grade. On the other hand, if the pigment exists as small agglomerates of spaced particles (Fig. 4.21b), then the distances between the agglomerates will change with PVC, but, to a first approximation, the distances between the individual particles will remain constant (because the TiO_2 particles in the agglomerates are frozen in place). This will not be exactly true, since the spacing between particles near the surfaces of two nearby agglomerates will change as the concentration of the agglomerates increases. Even so, the overall effect of PVC on crowding should be small.

For the agglomerate morphology, the opacity versus PVC curve in the region below the CPVC would be nearly linear, while for the individual particle morphology, there would be significant curvature in this part of the opacity versus PVC curve. Inspection of this curve for the highly treated grade, shown in red in Fig. 4.10c and reproduced in a larger format as Fig. 4.23, shows a nearly linear response of opacity to particle concentration for the highly treated TiO_2 pigment, consistent with the agglomerate morphology (Fig. 4.21b). In fact, a linear fit, with the constraint of passing through the origin, has an R^2 value of 0.986.

We will now shift our attention from comparing the two possible morphologies for the highly treated grade to comparing various aspects of the opacity versus PVC curves for the highly treated grade and a universal grade. As Fig. 4.23 shows, these curves cross one another at the CPVC value of the highly treated grade (PVC =

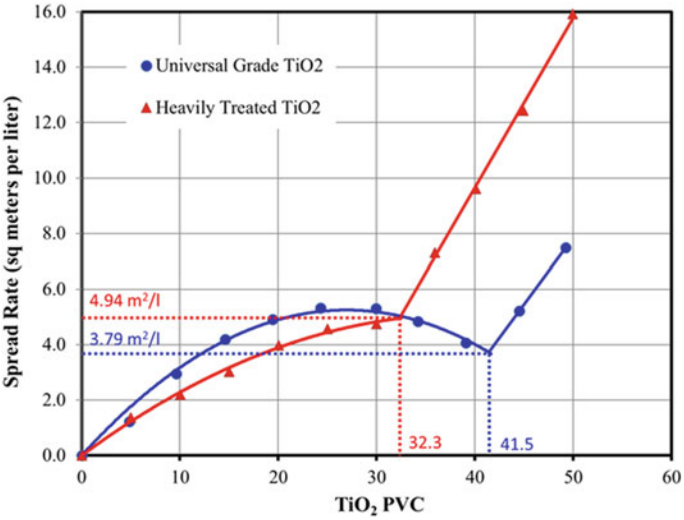

Fig. 4.23 Comparison of the opacity versus PVC curves for a universal grade of TiO_2 and a highly treated grade of TiO_2

32.3). The CPVC for the highly treated grade occurs when the TiO_2 agglomerates are packed as tightly as possible. At this PVC, the two paint systems have the same number of particles and the same paint opacities (spread rate = 4.94 m^2/l), indicating that the particles in both paints must have the same light scattering strength and so must have the same TiO_2 spacing. This spacing is the fixed spacing of the individual particles in the agglomerate.[27] Although this is the CPVC for the highly treated grade, the universal particles do not yet touch, and so their CPVC value should be higher, consistent with Fig. 4.23.

A second important aspect of Fig. 4.23 is that, below the CPVC value of the highly treated grade, we see that, at any given PVC value, these particles scatter light less efficiently than those of the universal grade (the red line in Fig. 4.23 is below the blue line at PVC values below 32.3), while above that CPVC we see the opposite. This is because, by fixing the particle–particle distances in the agglomerate, we are preventing the particles from spacing further apart below the CPVC, where there is room for the particles to spread into. This decreases the hiding below the CPVC. That is, when we compare the spacing of the TiO_2 particles for the two grades, the constant spacing of the highly treated grade is closer together than the universal grade below the CPVC of the highly treated grade, while the spacing is the same at that PVC and is further apart for the highly treated grade at PVC values above that PVC.

Finally, we see in Fig. 4.23 that the opacities of the two paint systems at their respective CPVC value are quite different. At its CPVC value (PVC = 32.3), the opacity of the heavily treated grade (spread rate = 4.94 m^2/l) is roughly 30% higher

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[27] We assume that at the CPVC condition, the distances between particles on the periphery of touching agglomerates are equal to the distances between particles within the same agglomerate.

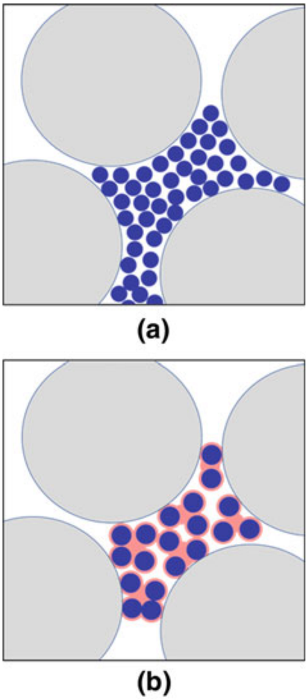

Fig. 4.24 TiO_2 particle packing conditions in paints formulated above the CPVC. **a** Universal grade of TiO_2. **b** Highly treated grade of TiO_2. Gray circles are large extender particles. Red regions are porous aluminosilicates. Blue circles are TiO_2 cores

than that of the universal grade (spread rate = 3.79 m^2/l) at its CPVC value (PVC = 41.5). In paints formulated above the CPVC, the TiO_2 particles are typically packed in the voids between the large extender particles at particle densities that are at or near their CPVC condition, as shown in Fig. 4.24. Since the highly treated particles give better opacity at their CPVC than do the universal particles at theirs, there is a significant advantage to using highly treated TiO_2 grades in paints formulated above the CPVC. This will be discussed in more depth in Chap. 16.

An extension of this analysis can be made by referring again to the universal pigment curve in Fig. 4.23. We see that the CPVC for this grade (41.5) is above PVC at the maximum in this curve (27.1). This means that decreasing the CPVC of the universal grade from its measured value will actually improve the hiding power of the paint. By replacing the universal grade with the highly treated grade, we are decreasing the CPVC and so should expect the hiding power to improve.

Oiled Hide

We can conceptually separate the factors that are responsible for increasing opacity as the PVC increases above the CPVC into two categories, both of which can be seen in Fig. 4.9b. The first are the two contributions from the air voids—scattering light in their own right and increasing the scattering strength of the TiO_2 particles. The second is the linear increase in the number of TiO_2 particles per unit area as the PVC increases.

It can be useful to separate these two contributions to increased opacity. In this way, the paint formulator can assess the effectiveness of the air voids. This effectiveness varies from one paint to another for several reasons, the most important of which is the size of the void [15]. This variability can be seen in the different slopes of the paint opacity versus PVC lines above the CPVC for different paint systems in Fig. 4.10.

We can separate these contributions by filling the air voids in the paint film of interest with mineral oil. The refractive index of mineral oil (1.47) is very similar to that of resin (typically from 1.48 to 1.55). This is not surprising since the two are similar chemically—they are both hydrocarbons, with the major difference between them being the length of the carbon chains, and this has little effect on refractive index. By replacing the air voids with mineral oil, we essentially return the film to the CPVC condition,[28] at least from a light scattering viewpoint.

The scattering strength of the paint film treated in this manner is termed the "oiled hide" of the film.[29] The average scattering power of the TiO_2 particles should be the same in all oiled films above the CPVC, regardless of the PVC, because the particles are in identical environments in all cases—packed as tightly as possible, and with the voids between them filled with hydrocarbon. The scattering power increases linearly simply because the film thickness and the number of TiO_2 particles per unit area increases as the PVC increases (Fig. 4.9b).

Because the average scattering power of the TiO_2 particles is the same in all oiled paints above the CPVC, we would expect them to be joined by a line that passes through the origin. This is in fact the case. In Fig. 4.25, we extend a line from the origin through the oiled spread rate values for the paints made with the highly treated TiO_2 grade in Fig. 4.10c. The correlation coefficient (R^2) for this line is 0.999, even with the constraint that it passes through the origin. Such excellent agreement between calculated and experimental values confirms the validity of the premise that the scattering volume overlaps between the TiO_2 particles in paints above the CPVC is constant.

Wet Hide

The hiding power of the wet film immediately after it is applied to a substrate is termed "wet hide" [16]. Although the film remains in this state for only a short time,

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[28] That is, the particles are packed as tightly as possible and the voids between them filled with hydrocarbon (resin in one case, a mix of resin and mineral oil in the other).

[29] In some regions of the world, this is instead called the "wet hide" of the film. We discourage this use of the term "wet hide" here as the same term is often used to define the hiding ability of the freshly applied wet paint, as discussed in the next section.

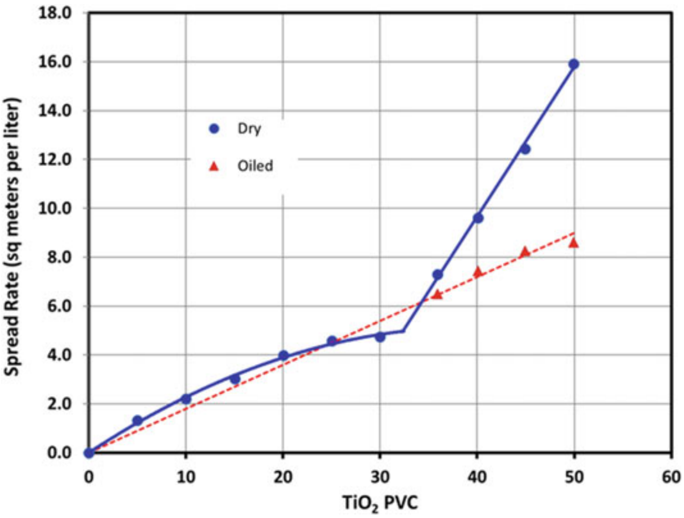

Fig. 4.25 Red triangles are the oiled hide values above the CPVC for a heavily treated TiO_2 in paints made with the same resin as in Fig. 4.10b, c. The red dashed line intersects the origin and so indicates a line of constant TiO_2 scattering efficiency [6]

its opacity is nonetheless of great importance for architectural paints (also called wall or décor paints). These paints are typically applied by roller, sprayer, or, less commonly, brush. In each case, the painter can control, within reason, the thickness of the paint applied.[30] The painter uses the opacity of the wet film as a guide in judging how much paint to apply onto the substrate for complete hide.

Ideally, the wet opacity and dry opacity of the paint would be the same, in which case the wet hide would directly indicate the amount of paint to apply. However, these two can differ significantly from one another in some paints. If the wet opacity is weaker than the dry opacity, then the paint is likely to be overapplied, resulting in waste. If the wet opacity is stronger than the dry opacity, then the paint is likely to be underapplied, requiring time and labor for the later application of a second coat.

Wet and dry opacity can differ from one another for several reasons. First, the particle concentration in the wet paint is lower than that in the dry film. This dilutes the TiO_2 particles, lessening the scattering volume overlaps and so increasing the opacity of the wet paint compared to the dry film. Second, in waterborne paints, the average refractive index surrounding the particles is lower in the wet paints (where this environment is dominated by water) than dry films (where this environment is dominated by resin). In addition, extender and resin particles scatter light when surrounded by water, although this scattering is not nearly as efficient as that of the

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[30] The lower end of the range of practical thickness is so thin that thickness variation due to the paint applicator (brush marks or, for roller application, stipple) results in visual non-uniformity across the wall. The upper end is dictated by the propensity of thick layers of wet paint to sag or run down vertical surfaces.

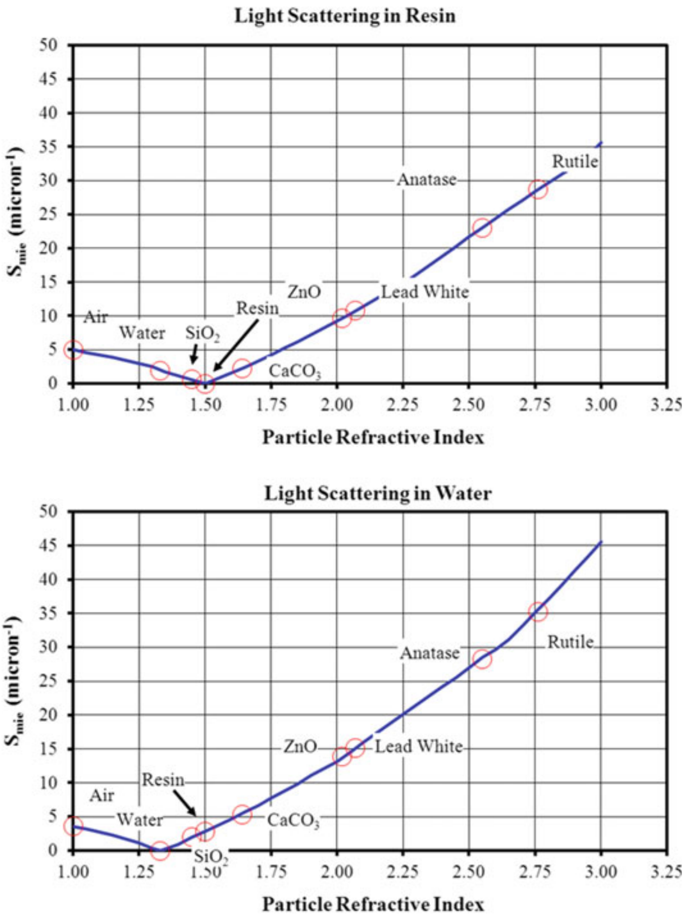

Fig. 4.26 Light scattering strength for particles typically found in paints, when surrounded by resin (top) and water (bottom) [6]

TiO_2 pigment [16].[31] The theoretical differences in the light scattering abilities of various paint components in the wet state versus the dry state are shown in Fig. 4.26 [6]. This figure indicates that TiO_2 content should be the primary determinant of wet hide, with minor contributions from extender particles. This has been confirmed experimentally [16].

These opacity losses on drying are offset in paints formulated above the CPVC, which many interior architectural paints are, by the presence of air voids in the

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[31] This is seen for clear lacquers, which are quite cloudy in the liquid state but completely transparent when dry, and with paints formulated below the CPVC with extenders only (deep base paints), which are also completely transparent when dry.

dry films.[32] This effect is so great that most paints formulated above the CPVC become more opaque on drying whereas paints formulated below the PVC become less opaque on drying.

Particle Size for Optimal Light Scattering

Before leaving the topic of light scattering in crowded systems, we will revisit the topic of TiO_2 particle size for maximum scattering. In Chap. 3, we calculated the optimal particle size for a single, isolated TiO_2 particle using two methods—the Mie equation and Weber's law. The results spanned a range from about 0.21 microns to 0.31 microns.

These results apply to systems that do not experience scattering volume overlap between particles (i.e., systems with PVC values below about 2.5). In systems where scattering volume overlap does occur, such as those described in this chapter, it does so between the parts of the scattering volumes that reside outside of the particles themselves. For this reason, the degree of scattering volume overlap is determined primarily by the surface-to-surface distance between particles. This distance depends on both the PVC and on the size of the particles, with smaller particles being closer to one another than the larger particles at the same concentration.

This is shown in Fig. 4.27 for two diameters of ideally spaced particles—one with a diameter of 0.23 microns and the other with a diameter of 0.26 microns (compare with Fig. 4.11, which is for a 0.25 micron diameter particle). We chose these diameters for discussion because in Chap. 3, in Fig. 3.8, we saw, using the Mie equation, that the scattering strength of a 0.23 micron TiO_2 particle is slightly greater than that of a 0.26 micron particle under conditions where there is no scattering volume overlap and so the 0.23 micron particle is preferred for plastic applications, where the PVC is so low that there is no scattering volume overlap.[33]

In Fig. 4.27, we see that the surface-to-surface distances for these particles overlap at the two ends of the PVC range, but not in the center of the range, that is, they deviate at the PVC values typically of interest to paint formulators. This has important implications for the optimal TiO_2 particle size for paints, as follows.

Consider paints made with each particle size at 15.0 PVC. The surface-to-surface distance for the smaller TiO_2 particles, if ideally spaced, is 0.164 microns, while that for the larger particles is 0.183 microns. For the paint system shown in Fig. 4.5, we can calculate that for this paint system the loss of opacity due to scattering volume overlap at 0.164 microns is 5% greater than at 0.183 microns, and so in this case we

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[32] The opacity of paints containing hollow sphere polymer pigments (described in Chaps. 7 and 10) also increases on drying because these spheres contain water in the wet state (and so do not scatter light) but contain air in the dry state.

[33] The 0.23 micron particle is also preferred because its undertone, which is bluer than that of the larger particle, offsets the slight yellow color of many polymers (see Chap. 2 for information on pigment undertone).

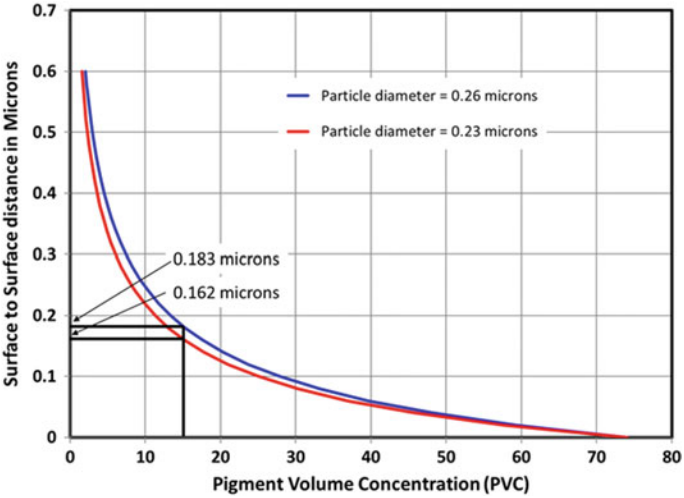

Fig. 4.27 Surface-to-surface distances as a function of particle concentration for two sizes of particles

would expect the larger particles to scatter light 5% more efficiently at 15.0 PVC than the smaller particles.

Overall we see, therefore, that the optimal particle size for TiO_2 light scattering is dependent on the concentration of the intended application, and that a larger particle is preferred at TiO_2 concentrations typical of paints than for those concentrations typical for plastics. In addition, we see that using the wrong particle size can result in a roughly 5% loss in opacity. Large TiO_2 producers are capable of controlling their particle size within this range and so produce different primary particles for different end-use applications.

Light Scattering in Paper Laminates

Paper laminates require a high level of opacity, and the papers used in them typically contain roughly 40% TiO_2 by weight. That said, because of the low densities of most paper ingredients, as well as the extensive pore structure of paper, this amounts to only about 10% TiO_2 by volume. As such we would expect particle crowding and scattering volume overlap to be relatively low. This is not the case, however, because the particles in paper are not distributed evenly throughout the sheet, but rather are found in small regions, or pockets, of high particle density. The effective PVC value within these pockets can readily exceed 50 and these particles are typically packed as tightly as at their CPVC condition.

There are two important consequences of this non-homogenous packing. The first is that the response of opacity to TiO_2 loading is generally linear, unlike what is seen in paints (e.g., Fig. 4.8). This is because increasing the loading of TiO_2 does not alter the amount of scattering volume overlap of the existing TiO_2—it alters the number of TiO_2 pockets, but not their local density. The second is that there is a significant opportunity to improve opacity by better spacing the particles when they are packed at their highest density. This will be discussed in more detail in Chap. 18.

Summary

Light scattering in systems containing more than 2.5 volume percent TiO_2, which includes most paints, is complicated by the negative effect that near neighbor particles have on one another's scattering strength. These effects are due to overlapping scattering volumes, which reduce the total scattering of the system. As particle concentration increases, the distances between particles decrease and so the scattering loss due to scattering volume overlap increases. At the same time, as the TiO_2 particle concentration increases, there are more scattering centers in the paint. As a result of these two opposing effects, the relationship between TiO_2 concentration and paint opacity is non-linear.

This relationship is most usefully expressed through a chart of paint opacity as a function of TiO_2 PVC. In such charts, the opacity increases steeply at low TiO_2 volume concentrations, where the particles are well separated and so do not suffer from scattering volume overlap. At roughly 2.5 PVC, scattering volumes begin to overlap, and the opacity benefit from increasing the number of scattering particles begins to decrease. This loss of effectiveness grows as more and more particles are added, and, at a certain point, increasing the particle concentration actually leads to a net loss of opacity.

This loss in opacity with increasing particle concentration continues until the paint arrives at its CPVC value, where the particles are crowded as densely as possible and there is just enough resin to coat the particles and fill the voids between them. As the PVC continues to increase, air becomes incorporated into the paint film. Air voids increase the film opacity because they can scatter light in their own right and because they improve the scattering efficiency of the TiO_2 pigment. However, these opacity improvements come at a cost in terms of paint properties—the air voids join together into a network of pores that reduce the strength of the film and degrade the protective properties of the paint on the substrate.

The presence of extender particles in a paint further complicates the relationship between TiO_2 content and film opacity. Both large and small extender particles cause the TiO_2 particles to crowd one another, but for different reasons. Large extenders exclude the TiO_2 particles from large regions in the film, while small extender consumes resin that would otherwise be used to space TiO_2 particles.

It is convenient to quantify these crowding effects through the effective TiO_2 PVC concept. To do this the equations used to calculate the TiO_2 PVC are modified to remove the volume of the paint that is inaccessible to the TiO_2 particles. In this way, we can compute the amount of scattering volume overlap in terms of the local concentration of the TiO_2 particles.

Although extender particles cause the TiO_2 particles to crowd together, and so decrease their scattering strength, they can have a beneficial effect on opacity as they can be used to bring a paint above its CPVC value. This could be done using TiO_2 pigment alone, but the particle concentrations needed to reach and exceed the CPVC value more than offset any economic benefit of improving opacity through the incorporation of air, which is free.

Using extender particles to exceed the CPVC results in cost savings beyond the opacity boost due to bringing air into the film—extender particles also replace relatively expensive resin with an inexpensive substitute. This benefit is maximized by formulating the paint to have a high CPVC value, which can be done by using mixtures of extender particles with different particle sizes. In such mixtures, the larger particles are packed as efficiently as possible, which results in the replacement of much resin, and the smaller particles pack in the voids between the larger particles, replacing the resin that would otherwise be there and further increasing the amount or resin replaced by extender.

Appendix

In this appendix, we will show the process for modeling the strength of TiO_2 scattering in paint films that contain large extender particles based on the scattering that we see for the same TiO_2 particles in an unextended paint. This allows us to predict the expected opacities of extended paints based on the measured opacities of unextended paints.

Basis for the model:

The opacity of a paint containing only TiO_2 and resin (which we will refer to as an “unextended paint”) is invariably greater than that of a similar paint for which a portion of resin has been replaced by large extender (which we will refer to as an “extended paint”). The opacity penalty for the extended paint is due to the loss of scattering efficiency per TiO_2 particle because the extender particles crowd the TiO_2 particles together, as discussed in the text.

It is useful to have a means of describing the degree of TiO_2 crowding in a paint. An obvious way would be by the TiO_2 concentration—the higher the TiO_2 concentration, the greater the crowding. We can therefore describe the degree of TiO_2 crowding in an extended paint with a certain PVC value based on the PVC value that would give the same degree of crowding in an unextended paint. As discussed in the text, the effective PVC describes this degree of crowding. For example, a paint with an actual TiO_2 PVC of 20 and large extender PVC of 40 would have an effective TiO_2 PVC of 33.3, as calculated by Eq. 4.9 in the text. This means that the scattering efficiency of the TiO_2 particles in the extended paint (at 20 PVC TiO_2) is the same as the scattering efficiency that the TiO_2 particles would have in an unextended paint at 33.3 PVC

TiO_2. Note that the opacity of the extended paint at 20 PVC TiO_2 will not be the same as the opacity of the unextended paint at 33.3 PVC TiO_2 (i.e., at the effective PVC) because, although the TiO_2 particles experience the same amount of crowding, there are more of them present in the unextended paint (since it is at a higher PVC).

In our model, we will develop a way to modify the opacities of the unextended paints by decreasing the scattering strength of each TiO_2 particle to reflect the opacity penalty of extender crowding in the extended paints.

Developing the model:

To demonstrate how this model can be developed, we will use the opacities of an unextended paint system to estimate the opacities of a paint system with 20 PVC large extender.

The model is based on experimentally determined opacity data for the unextended paint system. The first step in this process is to measure the spread rate (or another opacity indicator) of a series of unextended paints that span a range of TiO_2 values. Data for the paint system with the universal grade of TiO_2 that are shown in this chapter are given in the second column of Table 4.2 and plotted in Fig. 4.28.

Next, a measure of the scattering strengths per individual TiO_2 particle in these paints is calculated by dividing the spread rate (a measure of total scattering) by the TiO_2 PVC (a measure of number of TiO_2 particles). This is shown for the unextended paint in the third column in Table 4.2 and as the blue line and symbols in Fig. 4.29.

The best fit equation for this particular set of data is

$$\text{Scattering per unit concentration (unextended paint)} = -0.0063 \cdot \text{PVC} + 0.3634$$

We next calculate the expected line for the paint series with 20 PVC large particle extender. To do this we will define a factor F that is the ratio of the reciprocal of one minus the extender PVC when expressed as a fraction. In this case, F equals 1.25 $(=\frac{1}{1-0.2})$. Multiplying the actual TiO_2 PVC of the extended paints by factor F gives

Table 4.2 Scattering parameters for unextended paints below the CPVC

PVC	Measured spread rate (m^2/l)	Scattering per unit concentration[a]
0	0	–
4.9	1.55	0.313
9.6	2.89	0.300
14.6	4.15	0.284
19.4	4.91	0.253
24.3	5.32	0.219
29.9	5.29	0.177
34.2	4.80	0.140
39.1	4.11	0.105

[a] spread rate divided by PVC

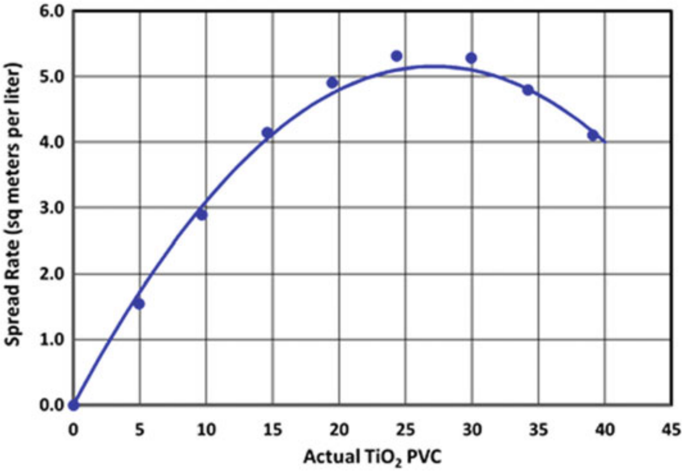

Fig. 4.28 Measured spread rate values for unextended paint system

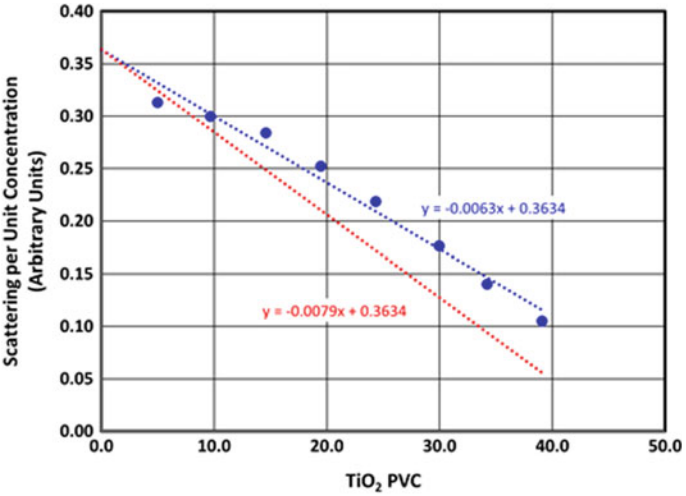

Fig. 4.29 Scattering per unit volume for the unextended paint series (blue) and calculated values for the 20 PVC extended paint series (red)

the effective TiO_2 PVC:

$$\text{Effective PVC } = \text{F} \cdot \text{PVC}$$

Because the scattering per unit concentration is linear with PVC, we can calculate the scattering per particle for the extended paint series as simply the scattering per particle at the effective TiO_2:

$$\begin{aligned}\text{Scattering per unit concentration (extended paint)} &= -0.0063 \cdot (\text{effectivePVC}) + 0.3634\\ &= -0.0063 \cdot (\text{F} \cdot \text{PVC}) + 0.3634\\ &= -0.0079 \cdot \text{PVC} + 0.3634\end{aligned}$$

This equation is shown as the red line in Fig. 4.29. We can use this line to predict the opacity values for the extended paints as a function of PVC by multiplying the scattering per unit concentration for the TiO_2 particles in the extended paints, as expressed in the equation above, by the actual TiO_2 PVC (that is, reversing the procedure used to develop Fig. 4.29 from Fig. 4.28). The results of this calculation are shown in Fig. 4.30.

This model is useful for calculating the expected opacity of paints made with extenders based on the opacity of paints made without extenders. In some situations, we may wish to do the reverse, that is, we may have measured the opacity versus TiO_2 PVC curve for a paint system that has extender in it and wish to calculate the opacity that the paints would have without the extender. One way of doing this is the reverse of the procedure discussed above, that is, to calculate the best fit line for the scattering per unit concentration for the extended paints, then adjust the slope of the line based on the effective TiO_2 PVC.

There is a second way to accomplish this task. To demonstrate this, we begin by plotting one data point from the opacity versus PVC curve for the extended paint that has 20 PVC large extender and 25 PVC TiO_2. This is shown as a red triangle in Fig. 4.31. We can extend a line from the origin, through this data point, and to the TiO_2 PVC of 31.25 (blue circle in Fig. 4.31). This PVC is the effective PVC value

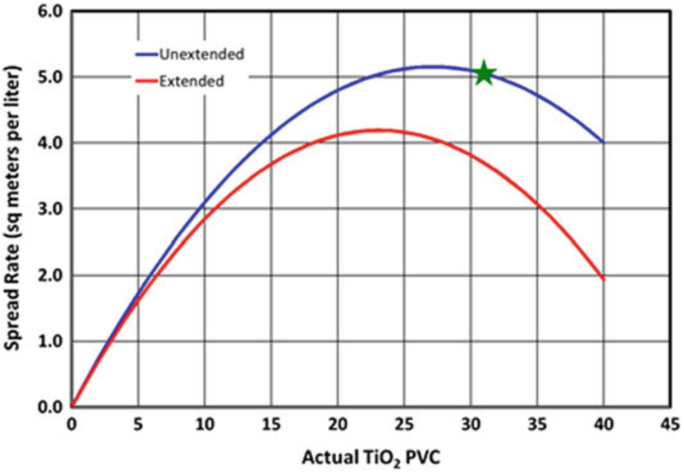

Fig. 4.30 Modeled opacity for extended paint system based on the opacity of the unextended paint system

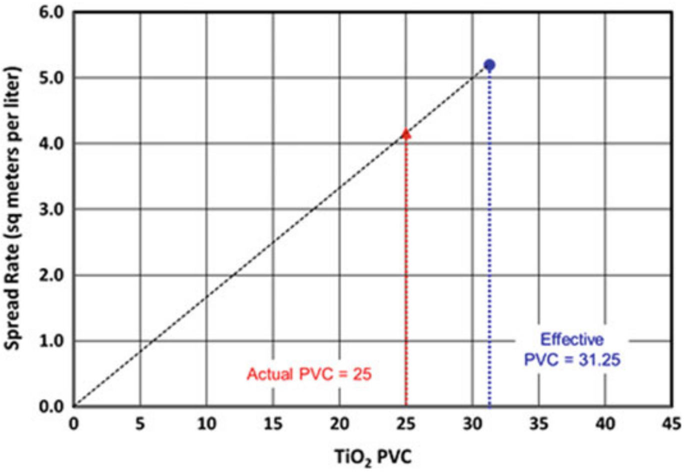

Fig. 4.31 Spread rate data points. Red triangle—extended paint at an actual TiO_2 PVC of 25. Blue circle—opacity of this paint at the effective TiO_2 PVC

of the paint and was arrived at by multiplying the actual PVC (PVC = 25) by factor F (1.25 in this case).

As explained in the text, all data points on the line going through the origin have the same TiO_2 scattering strength. The blue circle, therefore, indicates the same TiO_2 scattering strength as the unextended paint would have at a PVC of 31.25, and so this point will be a point on the curve for the unextended paint. For reference, this circle is indicated as a green star in Fig. 4.30.

We can repeat this process for any paint in the extended paint series to recreate the blue line in Fig. 4.30. However, in this case, the X-axis will be the effective PVC of the extended paint, rather than its actual PVC (note that the effective PVC values for the unextended paints equal their actual PVC). This is how Fig. 4.13b was created.

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