

---

## Overview

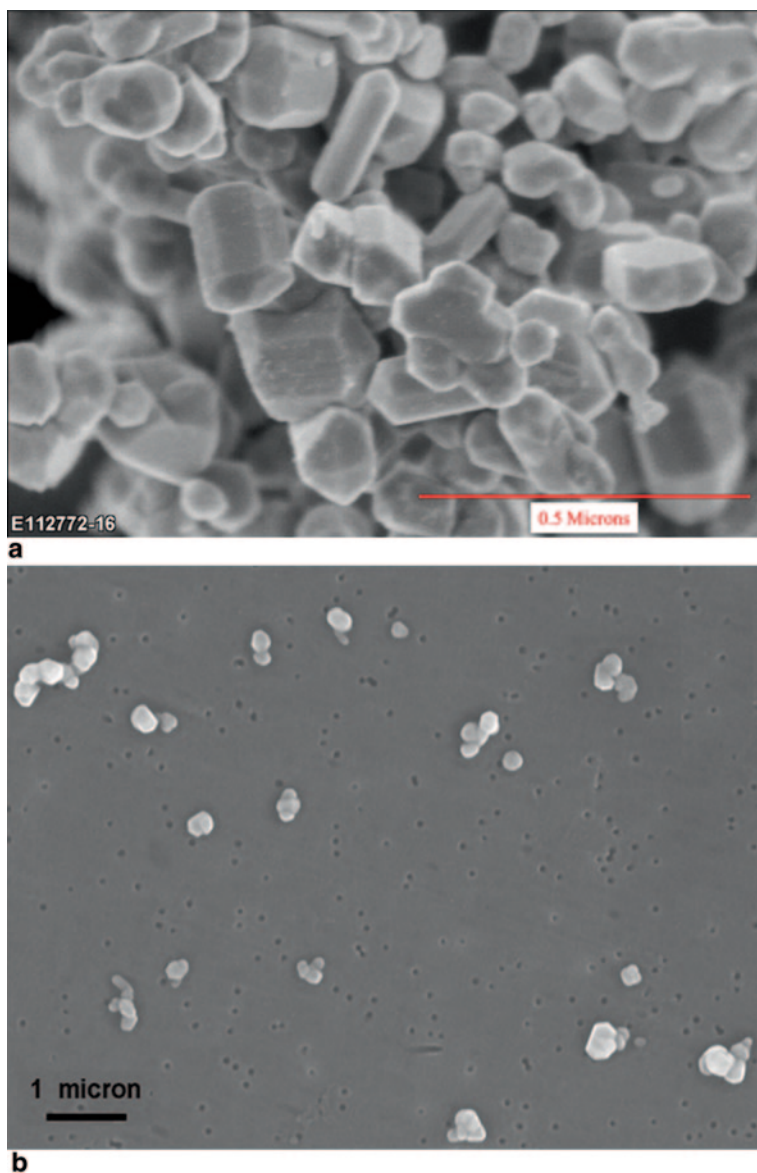
The interactions between light and groups of particles in paint films are highly complex. While we can accurately calculate the scattering of an individual photon by a single particle in a resin matrix, these results are difficult to scale-up to scattering by groups of particles in a paint film. This is due to a number of complicating factors, the most important of which is that particles that are separated by short distances interfere with one another's ability to scatter light. This phenomenon, termed "dependent scattering," occurs when the pigment particles are so concentrated that close contacts are unavoidable (crowding) or when liquid dispersions of particles, such as paint, are unstable and form flocculates or agglomerates (nonideal spacing). In this chapter, we review the dependent scattering phenomenon and describe ways of minimizing close pigment particle contacts and maximizing light-scattering from paint films.

---

## The Need to go Beyond Mie Theory

As described in the previous chapter, the light-scattering behavior of individual small particles embedded in a medium can, with some important restrictions, be calculated using a series of equations that were developed by Mie in the first decade of the last century. There are many constraints in these equations—for example, they are limited to single, spherical, isotropic particles—but, nonetheless, they can provide useful information about the properties of particles that affect light-scattering strength (the refractive indices of the particle and the medium, the size of the particle, and the wavelength of the light that the particle scatters). For materials commonly used in the coatings industry, maximum light-scattering is achieved using rutile  $\text{TiO}_2$  particles with diameters of roughly one-quarter micron.

On one hand, Mie theory is a very effective framework for understanding light scattering and so is an important tool for the coatings industry. On the other hand,



**Fig. 2.1** Typical morphology of pigmentary  $\text{TiO}_2$ . **a** High magnification showing the variety of shapes exhibited by chloride-process  $\text{TiO}_2$ . **b** Lower magnification showing the aggregate structure of these particles

however, its limitations prevent us from applying Mie results directly to paint films. One reason for this is that real pigment particles are much different than the ideal particles used in a Mie analysis. Real particles are rarely spherical (and can deviate greatly from it), often have different refractive indices in different crystal directions, come in a range of particle sizes rather than a single, optimal size, and are often joined together into aggregates (Fig. 2.1).

If these were the only differences between scattering based on ideal Mie particles and scattering of actual pigment particles in paint films, then we could account for these deviations by simply developing correction terms to the Mie equations. However, this is not the case. There are two additional phenomena that Mie theory does not account for, yet are critically important in determining the degree of light-scattering from a paint film. The first is multiple scattering, which is necessary for opacity, because most light that gets scattered by a single particle—even a strong scatterer such as  $\text{TiO}_2$ —is in fact only slightly deflected from its original path. In order for the light to reverse its direction and come back out of the paint film, it must undergo multiple scattering events.

The second phenomenon that cannot be accounted for in Mie theory is the loss of scattering power that occurs when two scattering particles approach one another. This phenomenon is termed “dependent scattering,” because, as we will see, the scattering efficiency of a particle depends on the environment around it. Losses due to dependent scattering can be quite large—there are many commercial paints for sale today that lose upward of 50% of the light-scattering ability of their  $\text{TiO}_2$  pigment due to this phenomenon. Before we discuss the implications of dependent scattering—and how to minimize it—it is useful to understand why it occurs.

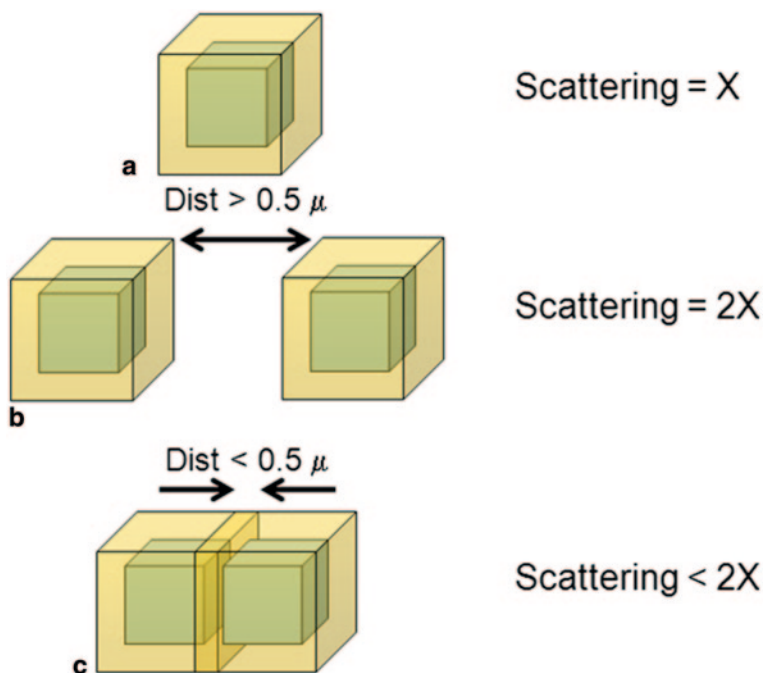
---

## Dependent Light Scattering

Intuitively, the amount of light scattered by a particle should be no more than the amount of light that strikes the particle and is not absorbed by it. After all, it seems logical that light not actually hitting a particle would not be affected by it. This is not the case, however. As shown in the previous chapter, the process of diffraction causes light that passes *near* a particle to be deflected as if it struck the particle. This leads to the curious situation that the light-scattering cross-section of a particle ( $C_{\text{sca}}$ ) can be larger than the physical cross-section of the particle itself. We can visualize this by imagining a region of space around a pigment particle that will scatter any light that enters it—whether or not the light actually strikes the particle. This scattering volume is shown in Fig. 2.2a.

Next, we consider the total scattering from two pigment particles. If the particles are far from one another (Fig. 2.2b), then each particle scatters light as if the other particle was not there, and the total light-scattering is simply twice the scattering of an individual particle. However, if the particles are brought closer together, so that their surfaces are within about  $0.5\ \mu\text{m}$  from one another, then their scattering volumes begin to overlap (Fig. 2.2c) [1]. Due to this overlap, the total scattering volume from the two particles is less than the sum of the two individual scattering volumes. Not only that, but light that enters the overlap volume actually scatters less efficiently than light that enters a part of the nonoverlapping scattering volume. Calculations show that the scattering from two  $\text{TiO}_2$  particles touching one another is only about 80% of that from two isolated  $\text{TiO}_2$  particles [2].

While a 20% opacity penalty for particles that touch is significant, it is in fact only the tip of the iceberg. When tightly packed, a  $\text{TiO}_2$  particle can accommodate 12 touching neighbors, and the opacity loss for a particle with this many close contacts exceeds 70% [3]. In situations where particles are apt to touch one another



**Fig. 2.2** Effect of particle separation distance on scattering volume overlap. Inner blocks are the  $\text{TiO}_2$  particles and outer blocks are the scattering volume. **a** Scattering =  $X$ , **b** Scattering =  $2X$ , **c** Scattering  $< 2X$

(either through flocculation or extreme crowding), it is quite likely that any given pigment particle will have multiple touching or nearby neighbors. Clearly, there is value to formulating paints for which this type of opacity loss is minimized.

## PVC and $\text{TiO}_2$ PVC

As our attention shifts from individual particles embedded in a matrix to groups of particles dispersed in a paint film, it is important to clearly define the method we will use to describe the concentration of these particles. Dry paint films consist of discrete, nonfilm-forming particles (pigment and extender) dispersed throughout a continuous matrix (the resin). The physical characteristics of these discrete/continuous systems are influenced greatly by the balance of volumes between these two phases, and for this reason the concentration of particles in a paint film is measured on a volume basis rather than the more usual ways of computing concentration—by weight per unit volume (g/ml) or by number per unit volume (mol/l).

The balance between the discrete and continuous components of the dry film is most conveniently reported as the pigment volume concentration (PVC) of the system, and is calculated as the volume of the discrete phase (the nonfilm-forming

particles) divided by the total volume of all solids (both the discrete and continuous phases)<sup>1</sup>; (see Eq. 2.1). PVC is normally expressed as a percentage, but, by convention, the percent sign (%) is omitted. In Chaps. 5 and 7, we will discuss extenders, which are nonscattering particles added to the paint. For the purposes of calculating PVC, extender particles are considered “pigment” (it is unfortunate that early workers defined the letter P in “PVC” to stand for “pigment”, when, in fact, it would have been more correct for it to stand for “particle”). When both extender and pigment particles are present in a paint film, it is sometimes useful to consider the volumetric concentration of just the  $\text{TiO}_2$  pigment, and we will refer to this as the “ $\text{TiO}_2$  PVC” (Eq. 2.2).

$$\text{PVC} = \frac{\text{Volume}_{(\text{TiO}_2)} + \text{Volume}_{(\text{All Extender})}}{\text{Volume}_{(\text{TiO}_2)} + \text{Volume}_{(\text{Resin})} + \text{Volume}_{(\text{All Extender})}} \quad (2.1)$$

$$\text{TiO}_2\text{PVC} = \frac{\text{Volume}_{(\text{TiO}_2)}}{\text{Volume}_{(\text{TiO}_2)} + \text{Volume}_{(\text{Resin})} + \text{Volume}_{(\text{All Extender})}}. \quad (2.2)$$

---

## The CPVC

There is a special PVC value—the critical pigment volume concentration (CPVC)—that merits additional attention. In paint films that do not contain air voids, we can conceptually divide the resin into three types. First, type 1 resin is present as a thin layer that coats each discrete phase particle (pigment and extender) [4]. These resin-coated particles can then be arranged in a closest-packing configuration, and the second category of resin (type 2) fills the voids or interstices between the tightly packed particles.<sup>2</sup> Finally, if there is more resin available than is needed to coat the particles and fill the interstices, the excess resin (type 3) finds itself between particles, pushing the particles further apart than they are when in their closest-packing arrangement by diluting them. This latter resin type is often called “free resin,” a designation that references its freedom to occupy any region of the paint film, rather than its cost.<sup>3</sup> Type 3 resin plays a valuable role in coatings, since it improves the scattering efficiency of the  $\text{TiO}_2$  particles by increasing their separation distance.

---

<sup>1</sup> Note that the volume of air voids, if present, is omitted from this calculation. The term “pigment packing factor”  $\phi$ , is used for the ratio found by dividing the volume of the particulates by the entire volume of a film including air voids. When no air voids are present,  $\phi = \text{PVC}$ . This is discussed in detail in Chap. 6.

<sup>2</sup> In the literature, the total amount of types 1 and 2 resin for a given paint, or, more precisely, for a given mix of particles, is referred to as the “resin demand” of that paint or particle mix.

<sup>3</sup> Free resin is, in fact, anything but free. As will be discussed later, replacement of relatively expensive free resin by an equal volume of inexpensive extender particles is an important method of decreasing the cost of a paint.

We can imagine making a series of paints containing only  $\text{TiO}_2$  and resin at different  $\text{TiO}_2$  concentrations (that is, different PVC values), from very low to very high. At the low end of the PVC series, we have only a few  $\text{TiO}_2$  particles dispersed in a large volume of resin. Here, we have all three types of resin as detailed above. One way to imagine increasing the PVC to the higher levels seen in the other paints in the series is to remove the resin from the low PVC paint, by decreasing the overall volume of the paint. The resin is not removed from the three resin types randomly or proportionally, but instead sequentially: The first amount removed is type 3 resin—excess resin between the particles. This has the effect of bringing the particles closer together as the paint compresses to fill the voids formed by the removal of this type of resin.

As we continue to higher PVC values by removing additional resin, the  $\text{TiO}_2$  particles eventually get as close to one another as is physically possible, meaning that we have exhausted the supply of excess (type 3) resin and that the particles are in their densest packed arrangement. To further increase the PVC, we must begin to remove type 2 resin—the resin that fills the regions between the tightly packed particles. This creates air voids in the film. This transition point is termed as the CPVC [5], and paints made above using the CPVC contain air voids.<sup>4</sup>

One might expect the CPVC of every paint system to be the same, since it seems reasonable that the CPVC point should be a geometric property of closest-packed particles and not specific to any one particle type. Indeed, the CPVC value for identical spheres packed in an ideal closest-packing arrangement is approximately 74, regardless of the size of the sphere.<sup>5</sup> In real world situations, uniformly sized spheres will be packed in a random close-packing arrangement, which results in a solid volume concentration of about 64. The packing arrangement of actual pigment particles, however, is far from this ideal, and a PVC value of 64 represents a starting point approximation for the actual CPVC.

The pigment and extender factors that can cause CPVC values to vary from paint to paint, fall into two broad categories: surface area and particle size uniformity. Surface area affects the CPVC because of the resin required to coat the surface of the particles (type 1 resin). The higher the surface area, the more type 1 resin is required by the particles, which results in a reduction in CPVC (that is, an increase in the resin concentration at the critical point). Particle size uniformity plays a role because small particles can fit in the interstices between larger particles. These small particles take the place of some of the types 2 and 3 resin that would otherwise fill the interstices, with the result that the CPVC value is increased (that is, there is a decrease in resin concentration at the critical point). We see, then, that actual CPVC values can be either above or below the random packing value, depending on the nature of the particles present in the paint. These concepts are discussed in more detail in Chap. 6.

<sup>4</sup> If we continue to even higher PVC values, we will eventually remove all of the type 2 resin. Going higher yet in PVC, we can only remove the layer of resin around the particles (type 1 resin). This resin holds the particles in the paint together, and, as it is removed, the paint loses all physical integrity.

<sup>5</sup> The exact value for this volume concentration is  $\frac{\pi}{\sqrt{18}}$ .

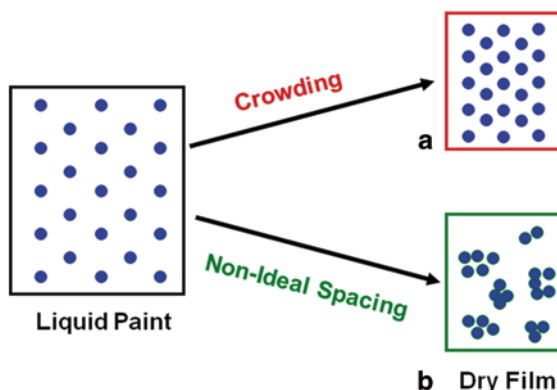
## Crowding Versus Nonideal Spacing

In most liquid paints, there are relatively few close particle–particle contacts. This is because the pigment particles are so diluted by the liquid carrier (typically water) that there is more than enough room to accommodate the particles without requiring close contacts. Furthermore, in well-formulated and well-dispersed paints, dispersant molecules attached to the pigment surface cause these particles to repel one another, ensuring good spacing between them.

The situation is different in the solid paint film, where there is no dilution liquid. The loss of liquid carrier during drying concentrates the pigment particles, resulting in close pigment particle–particle contacts, and overlapping of light-scattering volumes. This occurs by two independent mechanisms—particle crowding and nonideal spacing. These two phenomena are shown schematically in Fig. 2.3.

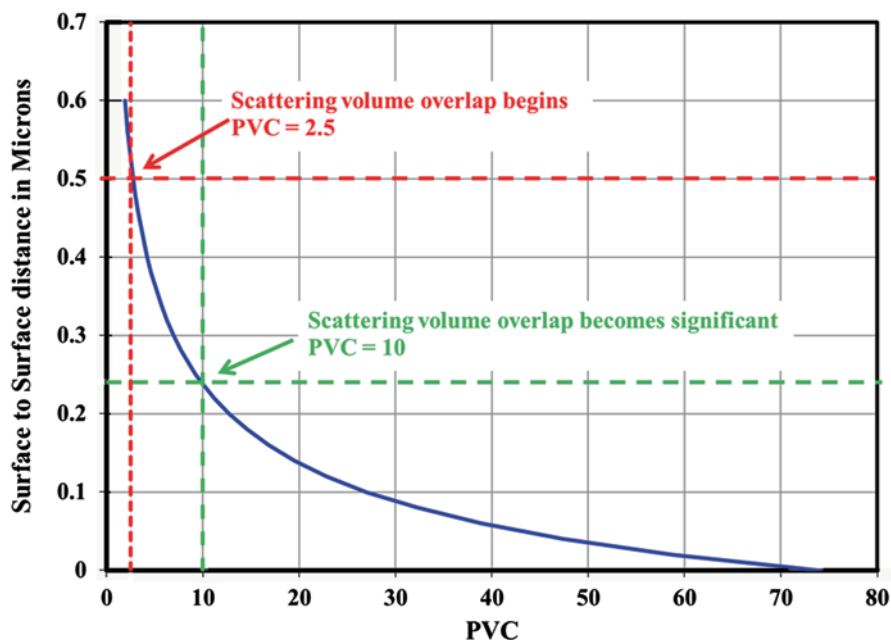
As the water (or solvent) in a liquid paint evaporates, the concentration of pigment particles increases substantially, leading to a decrease in average particle–particle distances compared to those in the wet paint (Fig. 2.3a). This decrease in particle–particle distances is referred to as “crowding” and is inevitable as a paint film dries. Based on theoretical calculations and geometric arguments, we expect crowding to first affect  $\text{TiO}_2$  light-scattering at  $\text{TiO}_2$  PVC values of a little less than 2.5, when the particle–surface separation is  $0.5\text{ }\mu\text{m}$ .<sup>6</sup> However, it is not until PVC values reach approximately 10 (surface-to-surface distances of roughly  $0.25\text{ }\mu\text{m}$ ) that crowding becomes great enough to have a significant detrimental effect on  $\text{TiO}_2$  scattering efficiency. At  $\text{TiO}_2$  PVC values above about 20, paint film scattering efficiencies are dominated by the negative effects of  $\text{TiO}_2$  crowding. Figure 2.4 shows the surface-to-surface distances of ideally packed pigment particles as a function of their PVC.

**Fig. 2.3** Types of close particle contacts: **a** Crowding; **b** nonideal spacing



<sup>6</sup> There is no sharp borderline that defines scattering volume, and, so technically, there is no cutoff interparticle distance above which there is no scattering volume overlap. That said,  $\text{TiO}_2$  pigment particles separated by more than  $0.5\text{ }\mu\text{m}$  experience essentially no scattering volume overlap.





**Fig. 2.4** Surface-to-surface distance as a function of PVC for perfectly spaced 0.25- $\mu\text{m}$  particles. Crowding begins at distances of 0.50  $\mu\text{m}$  ( $\text{PVC}=2.74$ ) and becomes significant at roughly 0.25  $\mu\text{m}$  ( $\text{PVC}=10$ ). Pigment volume concentration ( $\text{PVC}$ )

Crowding is one cause of scattering volume overlaps; nonideal spacing is the other. This term refers to deviations in particle spacing that occur due to particle–particle attractions or to the presence of large particles in the film (Fig. 2.3b). These two causes of reduced scattering intensity—crowding and nonideal spacing—are fundamentally different—crowding is inevitable as  $\text{TiO}_2$  PVC increases, but nonideal spacing is not. Whether caused by particle–particle attractions or by the presence of large particles, the defining factor of nonideal spacing is that the particles are not evenly spaced or distributed throughout the paint film. Nonideal spacing has many sources: The initial dispersion process might not be intense enough to break apart all of the pigment-particle agglomerates, the liquid paint may flocculate on storage, the changes in liquid environment as the water or solvent evaporates could cause dynamic flocculation during paint drying, and finally, as we will see, large particles will restrict  $\text{TiO}_2$  pigment particle access to portions of the dry film, forcing the pigment particles into small interstitial voids between the large particles. Regardless of the cause of nonideal spacing, its effects are identical to those described for crowding—loss of opacity due to overlapping scattering volumes. Once the source of nonideal spacing is identified, the paint chemist can often mitigate it through careful reformulation. Optimization of the paint manufacturing process can also provide beneficial effects in these situations.



## Light Scattering in Paint Films

We will discuss methods for controlling crowding and nonideal spacing below. Before we do so, however, we must discuss the equations that govern light-scattering intensity in paint films. These equations are very similar to the equations describing light absorption, and, for this reason, we will review light absorption as a model for understanding light-scattering.

In a typical light absorption experiment, a sample is prepared (usually as a liquid solution of a light-absorbing species) and illuminated with a strong light. Using a spectrometer, the loss in intensity of the light after passing through the sample is measured. We can understand this experiment by conceptually dividing the sample into very thin sections (Fig. 2.5a). Light that enters each section can do one of two things: be absorbed, or be passed on to the next thin section. The *fraction* of light that is absorbed is the same for all sections.<sup>7</sup> For this reason, the intensity of light decreases exponentially as it travels through the sample. The loss of intensity is typically reported as absorbance,  $A$ . Absorbance values span the range 0 (no absorption) through infinity (complete absorption).

The amount of light absorbed depends on the intrinsic absorption ability, or strength, of the absorbing molecule ( $\epsilon$ ), the concentration of this molecule ( $C$ ), and the path length of light traveling through the sample ( $l$ ). These quantities are related to one another by the well-known Beer–Lambert law:

$$A = \epsilon l C.$$

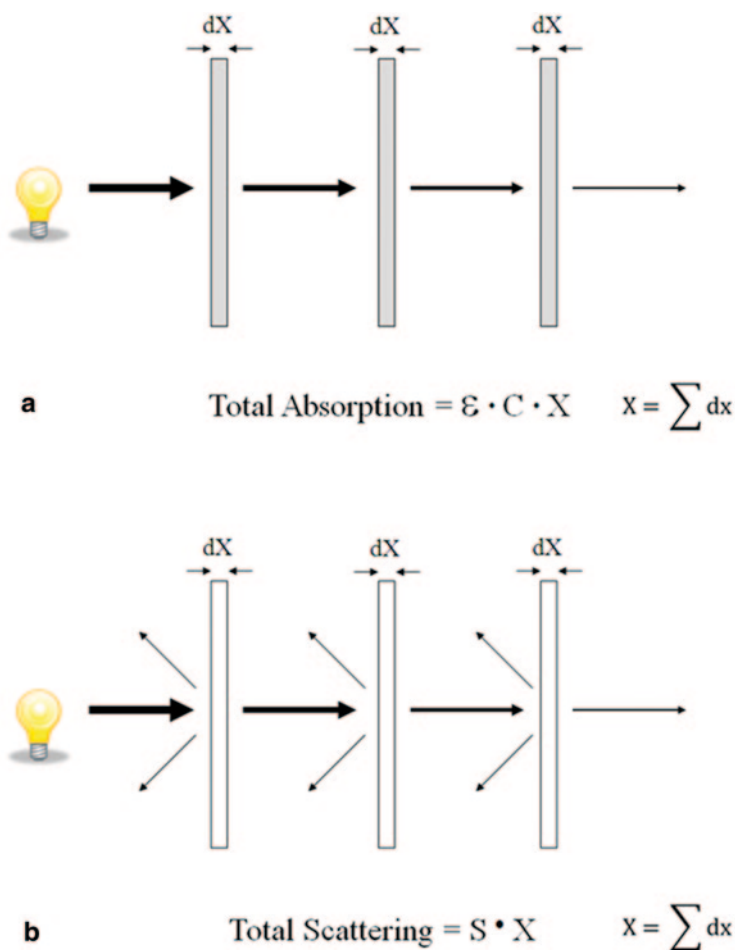
Here,  $\epsilon$  is termed the “molar absorptivity” of the light-absorbing material and is the amount of light absorbed by a thin section of sample at a standard concentration (typically 1 mol/l).

The light-scattering experiment is very similar to the light-absorption experiment except that the amount of light passing through the sample decreases due to scattering rather than absorption (Fig. 2.5b). An equation similar to the Beer–Lambert law exists for light-scattering:

$$\text{Amount of scattering} = SX.$$

In this case, there are only two terms on the right-hand side of the equation:  $S$ , which describes the amount of light scattered in a thin section of the sample, and  $X$ , the thickness of the sample (that is, the path length of the light). Like absorbance, the total amount of light scattered is a unitless number and spans the range from 0 (no scattering) to infinity (all light is scattered).  $X$  is normally given in distance units (usually mils or microns for paints), giving  $S$  units of inverse distance ( $\text{mil}^{-1}$  or  $\text{micron}^{-1}$ ).

<sup>7</sup> Each layer absorbs the same *fraction* of light, rather than the same absolute amount of light (number of photons). As light travels through the sample, its intensity decreases and so the absolute amount of light absorbed by the subsequent thin sections also decreases.



**Fig. 2.5** The light absorption (a) and light scattering (b) experiments

There are two related types of  $S$  values that are used extensively in the coating industry. One is the scattering efficiency of the film itself ( $S_{\text{coat}}$ ), while the other is the scattering efficiency of the  $\text{TiO}_2$  in the paint ( $S_{\text{TiO}_2}$ ). For  $S_{\text{coat}}$ , the thickness  $X$  used to calculate total scattering is the thickness of the paint film. For  $S_{\text{TiO}_2}$  the thickness  $X$  is the thickness of just the  $\text{TiO}_2$  portion of the film—in other words, the thickness that would be achieved if  $\text{TiO}_2$  particles were evenly stacked on top of one another until the number of particles per unit area is the same as the number of particles per unit area in the actual paint film. As will be shown in the next section, these two types of scattering efficiency are related to one another through the  $\text{TiO}_2$  PVC of the paint.

<http://www.springer.com/978-3-319-12014-0>

## Application of Light Scattering to Coatings

A User's Guide

Diebold, M.P.

2014, X, 196 p. 121 illus., 111 illus. in color., Hardcover

ISBN: 978-3-319-12014-0