H52: Pigmented Materials
Light Absorption and Particle Size

Introduction

In the two sections H52 and H53, the relationships between the optical properties of a pigmented material and the optical properties of the individual pigment particles are explored.

In Section H52, the following subjects are considered:

- The absorption properties of a single particle and the concept of "absorption efficiency" is introduced.

- The relationships between the properties of the single particles and the properties of a pigmented material.

The colour of a pigmented coating material depends on the types and amounts of pigments present in the material.

The colour also depends on the size of the pigment particles and how well the pigment particles are dispersed within the coating.

This relationship is illustrated by the result of a simple test of the state of dispersion, the "finger rub test", one of the QC tests described in section H26, "QC Tests for Colorants and Inks".

Example of a "Finger-Rub Test"

The test panel from a finger rub test of a paint that has a poor dispersion of the pigment particles is shown in Figure 1. In this paint, some of the pigment particles are present in loosely bound clusters, they are flocculates.

A few minutes after the application of the air-drying pigmented coating, the surface of the coated panel is gently rubbed by a finger, using a circular movement. The poorly dispersed clusters breakdown during the rubbing, this increases the level of dispersion in the rubbed areas by the break down of clusters into individual particles.

Figure 1: Finger rub test of the state of dispersion.

This results in an increase in the depth of colour in the rubbed region, as illustrated by the rubbed patches in the central region of Figure 1.
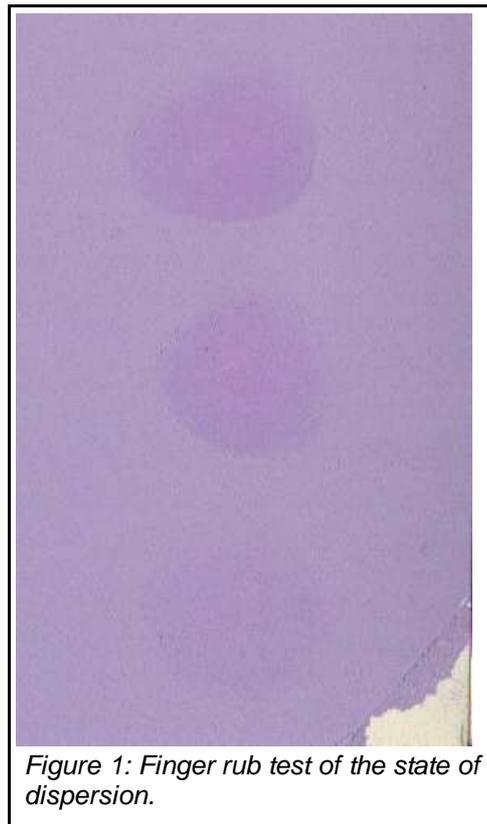
Light absorbed by a single particle

Each particle in a pigmented material may interact with the incident light. The interaction that occurs for an individual particle will depend on the intensity of the light and the surface area that the particle presents to the beam.

For particles of an irregular shape, the presented area depends on the orientation of the particle relative to the direction of the beam, as illustrated in Figure 2.
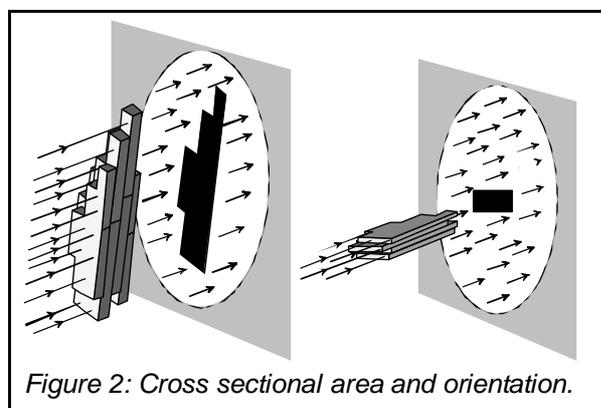

Figure 2: Cross sectional area and orientation.

It is usual to assume that the particles in a dispersion are randomly oriented and an average cross sectional area, A_{avg}, is used to represent the area that a particle presents to a light beam.

Power incident on a single particle ρ_{inc}

The power incident on a single particle ρ_{inc}, averaged over all orientations, is determined from the incident intensity (I_{inc}) multiplied by the area presented to the beam (A_{avg})

$$\rho_{inc} = A_{avg} \cdot I_{inc}$$

Power absorbed by the particle ρ_{abs}

The power absorbed by the particle ρ_{abs}, will depend on the optical properties of the particle. If the material is colourless and transparent then no light is absorbed. If the particle material is strongly absorbing, carbon-black for example, then almost all of the light may be absorbed.

The variation in absorption is characterised by defining an effective cross-sectional area, known as the absorption cross-section area C_{abs}.

It follows that the power absorbed by the particle is given by

$$\rho_{abs} = C_{abs} \cdot I_{inc}$$

The ratio of geometric area (A_{avg}) to the effective cross-section C_{abs}, describes the efficiency of the pigment particle at absorbing the incident light.

The absorption efficiency Q_{abs} of the pigment particles is defined as

$$Q_{abs} = \frac{C_{abs}}{A_{avg}} = \frac{\rho_{abs}}{\rho_{inc}}$$

Rearranging the equation provides the power absorbed by the particle

$$\rho_{abs} = Q_{abs} \cdot \rho_{inc}$$

Substituting $A_{avg} I_{inc}$ for ρ_{inc} gives;   Equation 52:1; $\rho_{abs} = Q_{abs} \cdot A_{avg} \cdot I_{inc}$

The absorption efficiency has no dimensions; it is the ratio of the effective cross-sectional area of the particle to the geometrical cross-sectional area.

The value of the absorption efficiency depends on

- The wavelength of the light The size of the particle
- The shape of the particle   The refractive indices of the particle
- The refractive indices of the surrounding material

Q_{abs}, dependence of absorption efficiency on particle size.

Fortunately, the way in which the absorption efficiency of a pigment particle changes with particle size is simple.

- The absorption efficiency starts at zero for zero size.
- For small particles compared to the wavelength of light, the efficiency increases linearly with the size.
- Beyond a certain size, which is dependent on the particle properties, the rate of increase starts to fall.
- Eventually the efficiency reaches an upper limit value of 1 or 100%. It then remains constant for further increase in the size.

Typical efficiency versus size relationships are shown in Figure 3 for three different types of pigment. The efficiency is determined for spherical particles that are surrounded by a colourless, transparent medium with properties that are typical for a paint medium and for a plastic.

The optical properties of the materials shown in Figure 3 are characterised by their refractive index (n) and attenuation coefficient (κ).

Material	Optical properties
Inorganic pigment	$n_1 = 3.00$, $\kappa = 0.05$
Organic pigment	$n_1 = 1.60$, $\kappa = 0.50$
Carbon black pigment	$n_1 = 1.60$, $\kappa = 1.00$
Medium	$n_0 = 1.50$, $\kappa = 0.00$

Small sized spheres

Some of the light that is incident on the surface is not reflected and will be transmitted into the sphere. For small spheres, the short distance travelled by the light within the sphere means that only part of the light is absorbed, the rest is transmitted out of the sphere and the absorption efficiency of the particle is much less than one.

Medium sized spheres

As the sphere becomes larger, more of the light passing into the sphere is absorbed because of the greater distance it travels. The absorption efficiency of the particle increases as the size increases.

Inorganic $n_1 = 3.0$, $\kappa = 0.05$

Organic $n_1 = 1.6$, $\kappa = 0.50$

Carbon black $n_1 = 1.6$, $\kappa = 1.00$

Figure 3: Absorption efficiency for different types of pigment

Large sized spheres

The distance travelled by the light within the sphere is so great that none of the light passing into the sphere is transmitted through it. The absorption efficiency has reached a constant, limiting value.

Large particle limit

Figure 3 shows that Q_{abs} trends towards a value of 1.0. However, this is not the correct limiting value for a large particle because only the fraction of the light that is not scattered by the particle can be absorbed.

For a large particle, scattering is by boundary reflection and the upper limit to the absorption efficiency is 1 minus the boundary reflection at the medium to particle interface.

The correct large particle limit is $\qquad$ *Equation 52:2*; $Q_{abs} = 1 - \left| \dfrac{m-1}{m+1} \right|^2$ Where $m = (n_1/n_0)$

Small particles (less than ~0.4 um)

### *Rayleigh's law of absorption*

For very small particles, smaller than the wavelength of light, Rayleigh determined an equation for the absorption efficiency of small spheres of radius r.

$$\text{Equation 52:3}; \quad Q_{abs} = 24\left(\frac{2\pi r}{\lambda}\right) \cdot \left[\frac{n^2 \kappa}{\left(n^2 + n^2\kappa^2\right)^2 + 4\left(n^2 - n^2\kappa^2\right) + 4} \right]$$

Rayleigh's absorption law has several consequences:

- The absorption efficiency of small particles is linearly dependent on their size. The efficiency increases with increase in particle size.
- For the same value of the attenuation coefficient κ, short wavelengths are absorbed more strongly than long wavelengths.
- The absorption efficiency is only weakly dependent on n, the real part of the refractive index ratio. This is not obvious from the form of *Equation 52:3*.

The Rayleigh equation applies to small particles only, particles with dimensions that are smaller than the wavelength of light.
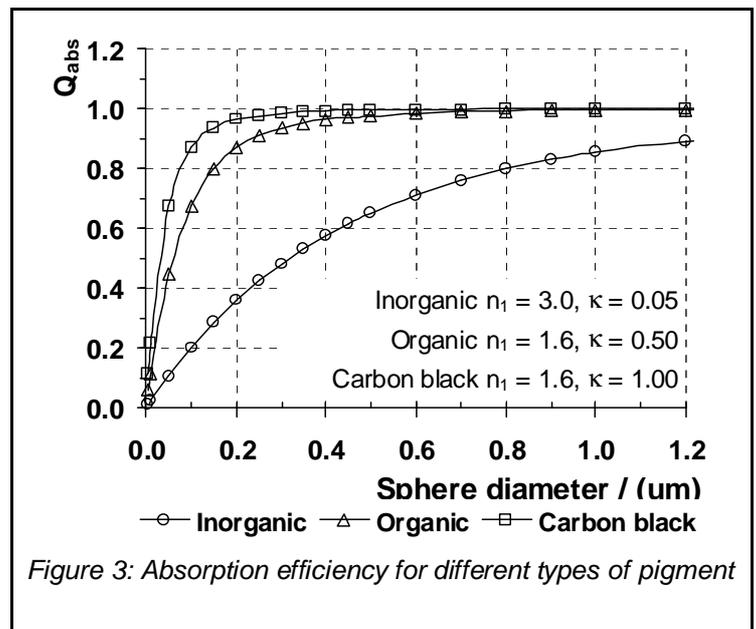
Medium to large size of particles (0.3 um to 6um)

Mie theory of absorption

The "anomalous diffraction" approximation to the Mie theory is used to estimate the absorption efficiency for the sizes of particle similar to the wavelength of light and larger. As shown earlier, Q_{abs} approaches a constant value for large particles, large compared to the wavelength of light.

The Mie equations reproduce the correct general shape for a plot of Q_{abs} against the size parameter but the magnitude of the Q_{abs} values are systematically in error.

$$\text{Equation 52:4;} \quad Q_{abs} = 1 + \frac{exp(-2\omega tan\,\beta)}{\omega tan\,\beta} + \frac{exp(-2\omega tan\,\beta) - 1}{2\omega^2\,tan^2\,\beta} \text{, and } tan\,\beta = \frac{n\kappa}{n-1}$$

Where ω is a dimensionless size parameter. $\qquad$ $\text{Equation 52:5;} \quad \omega = 2(n-1)\cdot\left(\frac{2\pi r}{\lambda}\right)$

Conclusions, single particles

It is possible to relate the optical properties of a particle of a material to the molecular properties by means of the refractive index n and the attenuation coefficient κ.

A study of the absorption efficiency of particles has shown that

- The absorption efficiency of particles much smaller than the wavelength of light is linearly proportional to their size.

- Above a certain size, the absorption efficiency of a particle is independent of the size of the particle.

- The absorption efficiency of particles depends on the attenuation coefficient of the material.

Absorption coefficient of a pigmented material

The primary definition of an absorption coefficient of a material is the parameter (ε) within the Lambert-Beer-Bougeur law. This law principally applies to light travelling within a coloured material that absorbs, but does not scatter light.

Lambert-Beer-Bougeur law absorption coefficient ($\mathcal{E}$)

Imagine a beam of collimated light (I_{inc}) passing through a thin slice within a material that does not scatter light.

The law proposes that the of the intensity lost by absorption (dI_{inc}) is proportional to the product of the intensity (I_{inc}), the absorption coefficient ε and the thickness of the slice (dx).

Intensity lost by absorption within the slice. $\qquad\qquad\qquad dI_{inc} = -I_{inc}\cdot\varepsilon\cdot dx$

The volume element (dv) involved in the absorption process, remembering that intensity has units of power per unit area, is given by $\qquad\qquad dv = (unit\,area = 1)\cdot dx$

It follows that the number of particles in the slice is $\qquad N\cdot dv = N\cdot(1)\cdot dx = N\cdot dx$

where N is the number of particles per unit volume of material.

From this we can obtain the power absorbed per particle · $\qquad$ $\text{Equation 52:6;} \quad \rho_{abs} = \frac{(I_{inc}\cdot\varepsilon\cdot dx)}{(N\cdot dx)}$

Equation 52:1 above, shows that the absorption power of a single particle is $\qquad \rho_{abs} = Q_{abs}\cdot A_{avg}\cdot I_{inc}$

Comparison of these two equations provides the absorption coefficient of a pigment dispersion (ε), in terms of the properties of the individual particles. $\qquad$ $\text{Equation 52:7;} \quad \varepsilon = Q_{abs}\cdot A_{avg}\cdot N$

Dependence of ε on particle size

It is well known that the tinting strength within the material of some types of pigment can increase dramatically during the milling and dispersion process. The absorption coefficient for a dispersion containing a fixed volume fraction V of mono-sized spheres is related to the particle size by the equation

$$\text{Equation 52:8;}\quad \varepsilon = Q_{abs} \cdot \frac{3V}{4r}$$

A dimensionless size parameter ($X = 2\pi r/\lambda$) can be used to separate the RHS of *Equation 52:8* into a size dependent term (Q_{abs}/X) and a volume fraction dependent term ($3\pi V/2\lambda$).

$$\text{Equation 52:9;}\quad \varepsilon = \left(\frac{Q_{abs}}{X}\right) \cdot \frac{3\pi V}{2\lambda}$$

Figure 4 shows the prediction of the way the absorption coefficient (ε) of a pigmented material depends on the diameter of the spherical pigment particles. The material contains a fixed volume fraction of pigment, so that the value of ($3\pi V/2\lambda$) is constant.

is a plot of (Q_{abs}/X) against particle size for a dispersion of three different types of spherical particles immersed in a medium of refractive index $n_0 = 1.50$.

The plots shown in Figure 4 are typical for:

Material	Optical properties
Inorganic pigment	$n_1 = 3.00$, $\kappa = 0.05$
Organic pigment	$n_1 = 1.60$, $\kappa = 0.50$
Carbon black pigment	$n_1 = 1.60$, $\kappa = 1.00$
Medium	$n_0 = 1.50$, $\kappa = 0.00$

Figure 4 shows that, in the limit of very small particle size, the absorption coefficient of the dispersion has a constant upper value.

For dispersions of particles of strongly absorbing materials such as organic pigments and carbon black, the coefficient remains constant with increase in size until, above a certain size, the absorption coefficient decreases with increase in particle size.

The rapid decrease for can be explained by noting that for these types of pigment, Q_{abs} rapidly approaches a constant value of nearly 1 as size increases.
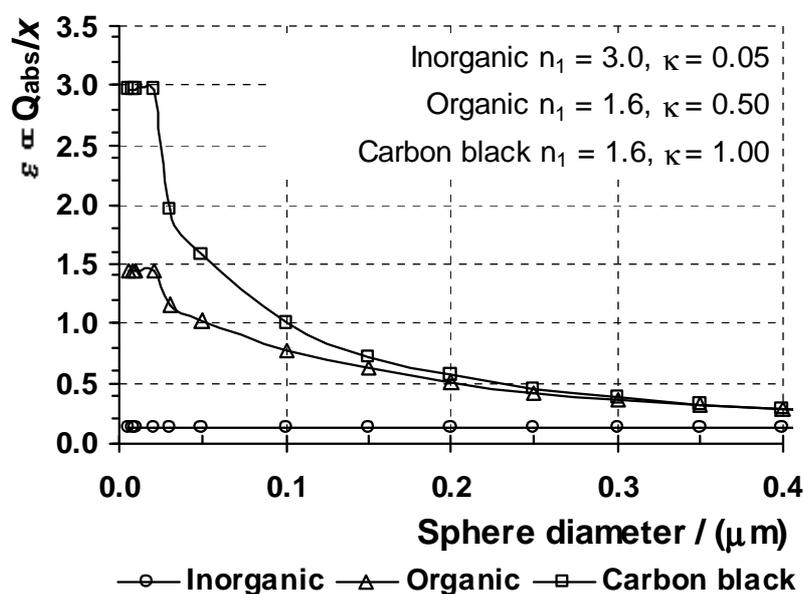

Figure 4: Absorption coefficient for dispersions of 3 types of pigment.

It follows from Equation 52:9, that when Q_{abs} is constant the absorption coefficient (ε) of the material will decrease as the particle size (r) increases in proportion to ($1/X$) = ($\lambda/2\pi r$).

According to Figure 4, the absorption coefficient of the dispersion of inorganic pigment does not change with particle size. This is a false impression created by the limited range of sizes shown in Figure 4.

Figure 5 is a plot of the absorption coefficient values of the dispersion of inorganic pigment over a wider range of sizes. The figure shows that the overall pattern of the size dependence for inorganic pigments is the same as that of organic pigments and carbon black.
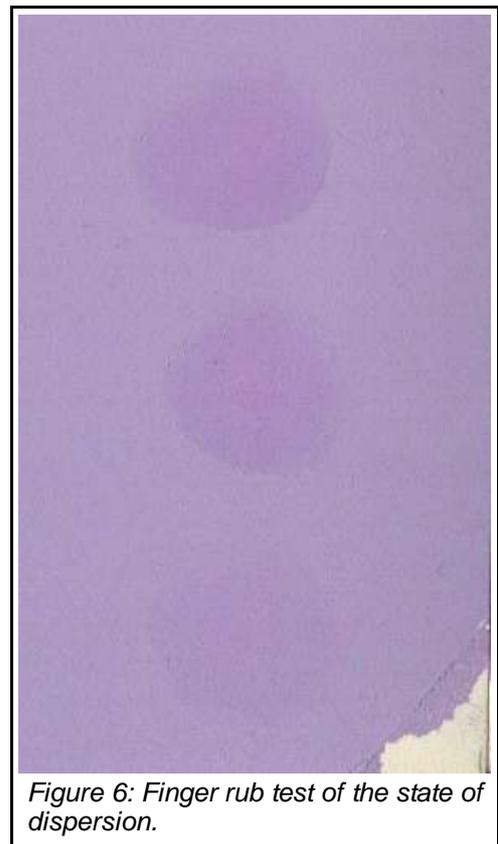

Figure 5: Absorption coefficient for a dispersion of inorganic pigment
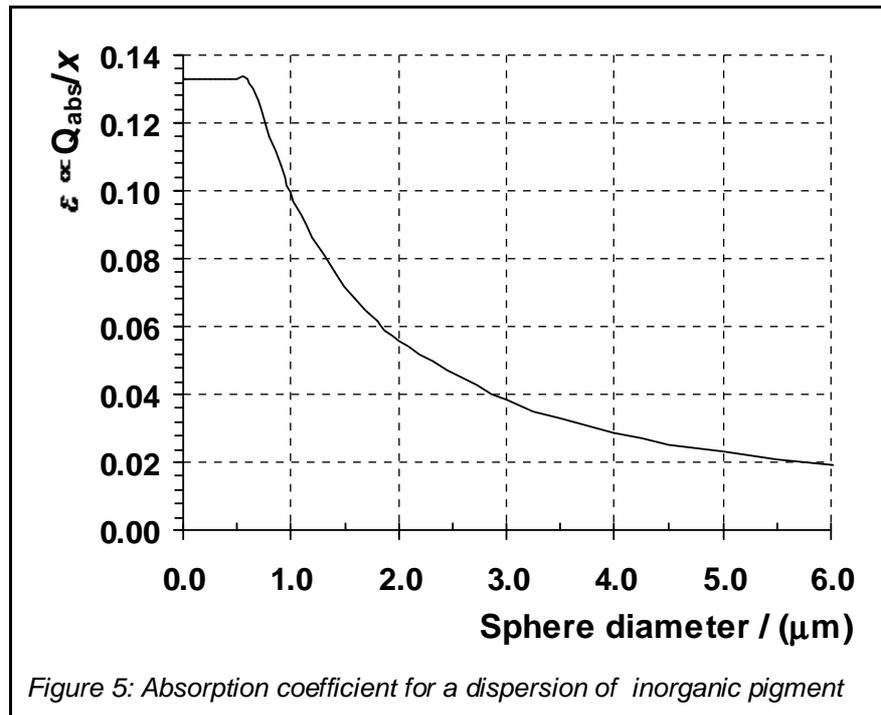
It is the absorption versus size relationship shown in Figures 4 and 5 that is apparent in the colour depth increase seen for a "finger rub test" panel when the test is applied to a poorly dispersed coating material.

Figure 6 is a copy of Figure 1, the test panel from a finger rub test of a paint that has a poor dispersion of the pigment particles. In this paint, some of the pigment particles are present in loosely bound clusters, they are flocculates.

A few minutes after the application of the air-drying pigmented coating, the surface of the coated panel is gently rubbed by a finger, using a circular movement.

The poorly dispersed clusters of pigment particles breakdown during the rubbing, this increases the level of dispersion in the rubbed areas. The smaller particle size results in an increase in the absorption coefficient in the rubbed areas and an increase in the colour depth.

Figure 6: Finger rub test of the state of dispersion.

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