Pigments are substances consisting of particles which are practically insoluble in the application medium. They are used to provide color but in addition can provide corrosion inhibiting, magnetic, electrical or electromagnetic properties. The range of application media for pigments includes paints, coatings, plastics, printing inks, construction materials, ceramic products, glass, enamel, and cosmetic formulations.

Pigments are differentiated and classified with respect to the way in which they interact with light. The most important pigment classes are:

- white pigments,
- colored pigments,
- black pigments, and
- effect pigments.

Fundamentally, all these pigments are employed because of their inherent ability to generate color. Effect pigments are classified simply as metal effect pigments or pearl luster pigments. Effect pigments are colorants that give additional color effects, such as angular color dependence (iridescence, color travel, luster) or texture, when applied in an application medium. The term “luster pigments” is also often applied to effect pigments because almost all effect pigments provide lustrous effects in practical applications. Luster pigments tend to be composed of predominantly platelet-like particles, that readily align with a parallel orientation to the surface to which they are applied. This leads to a characteristic luster arising from the reflection of incident light from the smooth surface of the pigment platelets.

The term “metal effect pigments” fully describes this class of effect pigments. However, “pearl luster pigments” does not give a comprehensive description of the diverse range of materials and effects provided by this class of effect pigments.

Metal effect pigments are luster pigments consisting of metallic particles only. In applications, with a parallel aligned orientation in their application system, they show a metal-like luster by reflection of light at the surface of the metal platelets. Pearl luster pigments on the other hand are luster pigments consisting of transparent or semitransparent platelets of metal oxides or other materials with high refractive index. They can also be applied with a parallel orientation to give a character-
istic pearl luster generated by multiple reflections. Pearl luster pigments showing additional colors generated by interference of light are also designated as nacreous or interference pigments \([1]\). Interference pigments are by definition effect pigments whose color is generated completely or predominantly by the phenomenon of interference of light \([1]\).

Various new effect pigments consisting of platelets of transparent materials have been developed in recent years. These pigments exhibit effects arising from multiple reflection followed by light interaction, but on the other hand they do not have a characteristic pearl luster. In addition, the class of effect pigments has been broadened by the development of interference pigments based on platelets of non-transparent materials. This has made the classification more complex and therefore the new term “special effect pigments” was created. This includes all platelet-like effect pigments, which can not be categorized as metal effect pigments \([2]\). According to this categorization, special effect pigments are pearl luster pigments and transparent and non-transparent interference pigments, which independent of their composition and structure lead to pearl lustrous or non pearl lustrous effects in combination with interference phenomena in the application medium.

Special effect pigments are natural or synthetic pigments, characterized by high luster, brilliance and iridescent color phenomena from optically thin films. The visual impression has its origin in reflection and refraction of the light at thin single and multiple layers. It is not limited in nature to pearls and clamshells as it can be seen in many fascinating examples in the world of birds, fishes, gemstones, minerals and insects. Fundamental investigations into the optical principles of the luster of natural pearls for instance shows that the brilliant colors are derived from layered and structured biopolymers formed by bio-mineralization \([3–5]\).

Figure 2.1 shows a comparison of the optical principles for the interaction of light with white, colored and black pigments, metal effect pigments and transparent interference pearl luster pigments.

White, colored and black pigments typically have particle diameters of 0.1 to 1 \(\mu m\). This encompasses the wavelength range of visible light. Some carbon black pigments have diameters even below 0.1 \(\mu m\). Effect pigments on the other hand have particle sizes predominantly in the range 5 to 100 \(\mu m\), in some cases also above these values. Therefore they have an average platelet diameter significantly larger than the wavelength of visible light. The thickness of the platelets, with some minor exceptions, is typically below 1 \(\mu m\), which is of the order to interfere with visible light. Effect pigments therefore have high aspect ratios (ratio of diameter to thickness), with values of up to 200.

White, colored and black pigments are mostly irregularly formed and predominantly interact with light as follows (Figure 2.1).
Figure 2.1: Schematic description of single particles of the types: (A) white pigment, (B) colored pigment, (C) black pigment, (D) metal effect pigment, and (E) pearl luster pigment in an application medium (e.g. paints, plastics, printing inks, cosmetic formulations). The typical interactions are shown, which lead in a large ensemble of particles to the below shown exemplary remission spectra (a–e). They are also the basis for classifying the pigments. (a) titanium dioxide (white), (b) chromophthal red, (c) carbon black, (d) aluminum (metal effect), (e) rutile on mica (interference red).
White pigments (A): The pigment particles completely scatter the incident light equally in all directions (diffuse reflection).

Colored pigments (B): The pigment particles absorb certain wavelengths of visible light and scatter the remaining wavelengths, depending on the color (selective absorption).

Black pigments (C): The pigment particles absorb all wavelengths of visible light (complete absorption).

Metal effect pigments (D) consist of thin metal (mostly aluminum) platelets; they are not transparent and reflect all incident light in one direction. The pigment particles act like small mirrors leading to a reflecting metal luster (metallic effect) when applied to give an aligned parallel orientation. Transparent interference pearl luster pigments (E) selectively reflect part of the light that is directly incident on the smooth platelet surface. The other part of the light enters into the transparent particles and is partially reflected either at interfaces within the pigments or at the bottom of the platelets. The internally reflected light leaves the platelets leading to interactions with adjoining pigment particles to create further reflections (multiple reflection). The partial reflection of light and optical superimposition create interference phenomena, which together with multiple internal reflections lead to the characteristic appearance of pearl luster pigments. The difference in refractive index between the high-refractive index pigment (typical values 1.8 to 2.9) and the application medium (the latter one has mainly values in the range from 1.5 to 1.6) is essential to the optical processes involved.

Pearl luster pigments can imitate the luster of natural pearls when the pigment layer and the paint layer structure are chosen in a suitable manner. Pearls and mother-of-pearl consist of a multitude of alternating transparent layers with different refractive indices. They have in most cases much larger lateral dimensions than in pearl luster pigments. The layers consist of calcium carbonate (CaCO$_3$) with a relatively high refractive index and proteins with a relatively low refractive index. The optical effects seen in pearls, mother-of-pearl and pearl luster pigments are similarly created by the interference of light rays, which are at least partly reflected at different interfaces.

Differences in the refractive indices of adjoining thin layers, particularly between pigment layers and the surrounding medium are a prerequisite for all iridescent colors arising from interference effects. Such effects are also well-known from the interfaces between air and an oil film or an oil film and a water surface. Similar differences in refractive index arise in the use of special effect pigments where the high refractive index platelet layers border upon the low refractive optically thinner application systems such as lacquers, printing inks or plastics. In applications, with a parallel aligned orientation of the platelets in the medium, by selective choice of
the layer thicknesses of the pigments the interference color and effects can be controlled in a manner suited to the wavelength of the incident light.

The basic types of pearl luster pigments are synthetic and natural pearl luster, interference pigments, transparent and partly absorbing. The pigments can consist of one layer (e.g. BiOCl) or of several layers with different refractive index (e.g. TiO$_2$ on mica). They can be made up of platelets with the same or varying thickness. In almost all cases, they are composed of crystalline layers (e.g. Pb(OH)$_2$ · 2 PbCO$_3$, BiOCl, TiO$_2$ on mica).

### 2.1 Optical principles

#### 2.1.1 Reflection and refraction at one and at several interfaces

The human eye can perceive objects only when electromagnetic waves with wavelengths in the range of 380 to 780 nm (visible light), which contain information about the objects execute analyzable color appeal. This is only possible when the object is emitting light by itself (self-illuminator) or when it is radiated from a primary light source and the incident light is thereby modified in regard of direction, intensity and spectral composition or of its phase (non-self-illuminator). The changes in the direction of light rays when striking an object with dimensions (l $>>$ $\lambda$) are described by the law of reflection and Snell’s law of refraction, whereby the refractive index of the medium that the light ray exits and that of the object that is entered must be different. According to Figure 2.2, the following optical laws have to be considered for the description of the light path:

- the law of reflection, where the angle of incidence $\epsilon$ and the angle of reflection $\epsilon'$ are identical
  \[
  (1) \quad \epsilon = \epsilon' \]
- and Snell’s law of refraction
  \[
  (2) \quad \frac{\sin (\epsilon')} {\sin (\epsilon'')} = \frac{n_1} {n_2} \]

The refractive indices $n_1$ and $n_2$ represent a relative measure of the velocity of light $v$ in the related medium. The refractive index of a vacuum is defined as $n_1 = c/v = 1$. Therefore the refractive indices of all other materials have values greater than 1, because the related light velocities always stay below the value in vacuum. Some examples of refractive indices of different materials are summarized in Table 2.1. The existing dependency of the refractive index from the wavelength of the light and from temperature can be neglected for these considerations. For a first approximation, it is possible to rely on averages or to use the values, which are effective for the perpendicular direction.
According to the law of refraction (2), the non-reflected part of the incident light (neglecting absorption and scattering) is deflected during the entrance in the optically denser medium in the perpendicular direction ($\varepsilon''<\varepsilon'$), see Figure 2.2. When light, on the other hand, is entering an optically thinner matter, the angle is enlarged in the perpendicular direction ($\varepsilon'' >\varepsilon'$).

Incident P1-P0, reflected P0-P2 and refracted P0-P3 light rays are always located in the same plane. Both laws are the result of the Fermat principle, which explains that the paths of the light rays between P1 and P2 respectively P1 and P3 are configured in such a manner that the light needs the least time to travel this distance.

Laws (1) and (2) are valid also in cases when the incident light rays arrive from different directions, the interface itself is formed irregularly and consists of non-ordered single elements ($d > \lambda$) or several boundaries in succession are not ordered in a plane-parallel manner. All of these cases can often occur separately or in combination (e.g. during diffuse illumination of paint surfaces, at paint surfaces with considerable unevenness and at paint layers with disoriented, preferably transparent and semitransparent interference.

Table 2.1: Refractive indices of various materials

<table>
<thead>
<tr>
<th>Medium</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacuum, air</td>
<td>1.0</td>
</tr>
<tr>
<td>water</td>
<td>1.33</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>1.37</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.42 to 1.48</td>
</tr>
<tr>
<td>plastics, paints, printing inks</td>
<td>1.4 to 1.7</td>
</tr>
<tr>
<td>mica</td>
<td>1.5 to 1.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.7</td>
</tr>
<tr>
<td>guanine, hypoxanthine</td>
<td>1.85</td>
</tr>
<tr>
<td>basic lead carbonate</td>
<td>2.0</td>
</tr>
<tr>
<td>bismuth oxychloride</td>
<td>2.15</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (magnetite)</td>
<td>2.4</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>2.5</td>
</tr>
<tr>
<td>TiO$_2$ (rutile)</td>
<td>2.7</td>
</tr>
<tr>
<td>$\alpha$-Fe$_3$O$_5$ (hematite)</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Figure 2.2: Schematic description of the direction of the rays after light reflection and light refraction at the interface, which divides two media with the refractive indices $n_1$ and $n_2$, $\vec{I}$, $\vec{R}$ and $\vec{T}$ are the direction vectors of light extension in the incident, the reflected and the refracted ray. $\vec{N}$ is the perpendicular vector of the interface.
pigments) and lead to a “diffuse reflection”. However, the light rays are now not more necessarily located in one plane and the directions of propagation of the light rays are described as vectors in space (see designation in Figure 2.2) with the corresponding law of reflection

\[ R^r = 2N \cos(\varepsilon) + I \]

and with the law of refraction

\[ T^r = \left( \frac{n_1}{n_2} \right) I - \left( \cos(\varepsilon'') - \left( \frac{n_1}{n_2} \right) \cos(\varepsilon') \right) N \]

(see Figure 2.2 as well).

When the illumination of the object is by many light rays at the same time, the limiting cases, which have to be distinguished are either the completely non-directed (diffuse) or the completely directed incident radiation. Diffuse illumination reflected at a plane interface remains diffuse. Directed illumination, on the other hand, is reflected diffuse when the interface is formed irregularly, is consisting of non-ordered single elements or when the light is deflected by scattering processes.

Figure 2.3: Schematic description of the borderline situations for the reflection respectively the scattering of light: (a) perfect mirror (mirror reflection), (b) perfect diffuser (only light scattering), (c) real surface (the reflection indicatrix exhibits a geometric form defined by scattering and reflection processes).
The comparison of different materials with different interface structures shows that rough, uneven surfaces reflect light rays diffusely in all directions. On the other hand, even surfaces reflect in the ideal case all light rays in one preferred direction. There are in practice, e.g. in paint systems, flowing transitions between situations a) (perfect mirror, high reflection coefficient) and b) (perfect diffuser, lowered reflection coefficient compared with a) described in Figure 2.3. Shape and size of the reflection indicatrix, in other words of the spatial spectral intensity distribution of the reflected radiation, include now all relevant reflection characteristics of the sample, which have their origin in scattering and reflection at the various boundaries – starting from the clear varnish to the pigment particles located deep in the system that can still interact with incident light.

The reflection coefficient \( r(\varepsilon) \) is now defined as the ratio of the reflected light intensity \( I_R \) to the incident light intensity \( I_E \) while the gloss \( G \) is determined as the ratio \( r_g \) (sample)/\( r_g \) (perfect diffuser) in the specular direction.

High gloss values are therefore also the reason for the strong and angle-dependent brightness, which not only appears at polished metal surfaces but also at boundaries of transparent bodies.

The reflection of directed light on even non-metallic surfaces (pure regular reflection) can be formulated mathematically using Fresnel’s reflection coefficient \( r(\varepsilon) \). Its description for non-polarized light is expressed by the following equation:

\[
(5) \quad r(\varepsilon) = \frac{I_R}{I_E} = \frac{1}{2} \left( \frac{\tan^2(\varepsilon' - \varepsilon'') + \sin^2(\varepsilon' - \varepsilon'')}{\tan^2(\varepsilon' + \varepsilon'') + \sin^2(\varepsilon' + \varepsilon'')} \right)
\]

Figure 2.4 illustrates the relationship between the reflection coefficient \( r(\varepsilon) \) and the angle of incidence \( \varepsilon \) for non-polarized light at \( n_2 = 1.5 \) and \( n_1 = 1 \). For angles of incidence below 30°, the values for \( r(\varepsilon) \) are almost constant at 0.04. For this reason, in this range the simple equation for light, arriving from the perpendicular direction (\( \varepsilon = 0^\circ \)), can be used

\[
(6) \quad r(0^\circ) = \left[ \frac{n_2 - n_1}{n_2 + n_1} \right]^2
\]

That means that a luminous flux coming from air at almost vertical contact with water will be reflected by 2%, with lacquer by 4%, with basic lead carbonate by 11%, and with rutile by 21%. Figure 2.5 just shows this dependency \( r(\varepsilon = 0^\circ) \) as a function of \( n_2 \) at \( n_1 = 1 \).

Only the difference in refractive indices is important for the size of the reflection coefficient, regardless whether the luminous flux comes from a more or less dense medium. If the second medium has a higher refractive index, the sign of the electrical field vector changes for the reflected part of the light, i.e. the light is shifted by
Figure 2.4: Reflection coefficient $r(\varepsilon)$ as function of the angle of incidence $\varepsilon$ at $n_2 = 1.5$ and $n_1 = 1.0$ (according to equation (5))

Figure 2.5: Reflection coefficient $r(\varepsilon = 0^\circ)$ as function of the refractive index $n_2$ at $n_1 = 1.0$ (according to equation (6))
half a wavelength in phase length. At interfaces to substances with a lower refractive index no phase shift takes place. This phase shift for reflection at optically denser media plays a significant role also for the interference behavior of layers.

Generally speaking, only a small part of the light meeting the interface will be reflected, the majority enters the next medium or passes through it. If the initial luminous flux $I_E$ is 1, then the reflected flux $I_R$ is given by the reflection coefficient $r$. If the light continues through a fully transparent and clear medium and then meets another interface, the principle occurring on the first interface repeats itself. The light intensity striking the second interface is now of course already diminished by the reflection at the first interface. Therefore the reflection coefficients of the interface order $k$, $r(k)$ relates to that in the first interface as

$$ r(k) = 1 - (1-r)^k $$

The following equation describes the situation considering multiple reflections between $k$ parallel interfaces:

$$ r(k) = \frac{kr}{1+(k-1)r} $$

Figure 2.6: Reflection coefficient $r(\varepsilon = 0^\circ)$ with a growing number of interfaces in a stack. The upper curve is calculated according to equation (7), the lower curve according to equation (8). The curves correspond calculations without and with multiple reflections at a stack of $k$ optically not coupled interfaces.
The resulting increase of the reflected light intensity with a growing number of interfaces (for the case \( \varepsilon = 0 \)) is shown in Figure 2.6. For effect pigments, the value \( k \) is of course even-numbered.

### 2.1.2 Pearl luster and interference effects

Natural pearls are made up of recurrently alternating layers of transparent mediums with differing refractive index. They are layers of calcium carbonate (aragonite, \( n \approx 1.7 \)) and protein (\( n \approx 1.4 \)). Thus, a very narrow ray of light that lands on the surface is reflected in such a way that it obeys the laws of reflection, but at the same time is diffused and gives the impression of gradually reducing intensity. To the eye, the luster takes on a three-dimensional character, because at times it seems to come from inside the object. This effect is increased by the rounded shape of the pearl. In summary, these effects are referred to as “pearl luster”.

A further phenomenon, which occurs with pearl luster pigments, is the interaction of light waves through the phenomenon of interference. Figure 2.7 is a schematic representation of this and should help in understanding the following explanation.

If a plane-parallel layer with a refractive index of \( n_2 \) is situated in a medium with a different density, then \( n_1 = n_3 \). It has already been mentioned that a light ray (L),

![Figure 2.7: Schematic diagram showing the phase relationships of interfering light rays (L1 and L2). The “detour” for L is AD + DB – CB.](image-url)