**Iron oxide red pigments**

Colouring inorganic pigments is commonly produced by a combination of light absorption and diffusion in the visible spectral range. The tests performed were carried out on phase-pure iron oxide pigments that are grouped together with selected properties in Table 1. α-Fe₂O₃ pigments have the crystal structure of the corundum and contain only octahedrally coordinated Fe(III) ions in a high-spin state, i.e. all five 3d electrons are unpaired, which is particularly important for the electron structure and thus the colouring.

The products exhibit a virtually isometric habit (spherical to cube-shaped). Average particle diameter varied in a range from around 0.08 to 1.0 µm. The smallest unit in oxidic iron(III) materials is formed by Fe(III)O₆ octahedra, each with six identical Fe-O distances of around 2.05 Å. Fe₃O₄ double octahedra with common faces are present in the hematite lattice, with the Fe(III) ions occupying only 2/3 of the available octahedron positions, while the oxygen lattice section is full. As a result of the unoccupied Fe(II) positions, a deficit in positive charge is produced that is compensated by moving the Fe(III) ions from the centre of the octahedra. This leads to pronounced distortion for the two individual octahedra (trigonal components). As a result, the Fe-O distances vary greatly (3 x 2.12 Å and 3 x 1.95 Å in the respective individual octahedron) and the Fe(III)-O-Fe(III) angle is approximately 85°.

**Light absorption and colouring**

When considering a hematite single crystal and a powder α-Fe₂O₃ pigment, in both cases the green and blue spectral ranges of the incident light are absorbed selectively. The unabsorbed proportion of visible light (600 – 720 nm) causes the red colour impression.

To investigate selective light absorption without influence from light diffusion, the absorption spectrum of a hematite single crystal was first recorded at room temperature (RT) and is shown in Figure 1. [2] The x axis shows the wave number (in cm⁻¹) and wavelength (in nm) and provides the energy positions of the absorption bands.

The y axis shows extinction E and enables quantitative data relating to the intensities of the absorption bands. The precise band position can be calculated using MO theory. [5]

**Table 1. Tested iron oxide pigments with selected properties**

<table>
<thead>
<tr>
<th>Pigment type*</th>
<th>Chemical composition level of the iron</th>
<th>Lattice type</th>
<th>Structural features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide red (hematite)</td>
<td>α-Fe₂O₃ (Fe(III) ions)</td>
<td>Corundum (α-Al₂O₃)</td>
<td>Fe₂O₃ double octahedra with common faces</td>
</tr>
<tr>
<td>Iron oxide yellow (goethite)</td>
<td>α-FeOOH (Fe(III) ions)</td>
<td>Diaspore (α-AlOOH)</td>
<td>Edge-sharing Fe₆O₉(OH)₃ octahedra</td>
</tr>
<tr>
<td>Iron oxide orange (lepidocrocite)</td>
<td>γ-FeOOH (Fe(III) ions)</td>
<td>Boehmite (γ-AlOOH)</td>
<td>Edge-sharing Fe₆O₉(OH)₃ octahedra</td>
</tr>
<tr>
<td>Iron oxide black (magnetite)</td>
<td>Fe₃O₄ (Fe(II) and Fe(III) ions)</td>
<td>Inverse spinel</td>
<td>Fe(II)/Fe(III) octahedra</td>
</tr>
</tbody>
</table>

* Phase purity was determined using the XRD method

---

Technical Paper

Inorganic pigments

Peter Köhler
Jürgen Kischkewitz

Synthetic iron oxides are an important group of inorganic colour pigments, with annual consumption around one million metric tonnes. But even though these products have been used extensively their colouring mechanism (causes of colouring) has not been described sufficiently to date. Detailed descriptions of colouring for red, yellow, orange and black iron oxides is provided and explained, using structural features of each and findings from ligand field and molecular orbital (MO) theory.

**Establishing the causes of colouring in iron oxide pigments**

When considering a hematite single crystal and a powder α-Fe₂O₃ pigment, in both cases the green and blue spectral ranges of the incident light are absorbed selectively. The unabsorbed proportion of visible light (600 – 720 nm) causes the red colour impression.

To investigate selective light absorption without influence from light diffusion, the absorption spectrum of a hematite single crystal was first recorded at room temperature (RT) and is shown in Figure 1. [2] The x axis shows the wave number (in cm⁻¹) and wavelength (in nm) and provides the energy positions of the absorption bands.

The y axis shows extinction E and enables quantitative data relating to the intensities of the absorption bands. The precise band position can be calculated using MO theory. [5]
A quantitative evaluation of all electron transitions of Fe(III)O₆ octahedra is possible using ligand field theory and provides the electron structure of α-Fe₂O₃ in the d⁵ multiple electron system. Figure 6 shows the simplified term structure with the measured (I and II) and calculated (III to VII) electron transitions in the visible spectral range. [6]

Unlike single crystals, both absorption and scattering properties need to be taken into account to explain colouring for powder iron oxide red pigments. When measuring pigment powders, the part of the light that provides colour (red spectral range) is first scattered several times on the pigment particles and then enters the spectrometer (integrating sphere) as diffused light. To obtain the absorption spectrum from the remission spectrum thus measured, the measured remission values R (α, λ) need to be converted using the Kubelka-Munk equation:

$$K = \frac{(1-R\alpha)^2}{2R\alpha}$$

and plotted against the wave number / wavelength as K/S.

**Results at a glance**

- Colouring inorganic pigments is commonly produced by a combination of light absorption and diffusion in the visible spectral range. Tests performed were carried out on phase-pure iron oxide red, yellow, orange and black pigments using structural features of each and findings from ligand field and molecular orbital (MO) theory.

- For iron oxide red pigments, rises in absorption become much less intense as particle size increases, and the steepness is reduced. A slight shift toward lower wave numbers also occurs. These changes result in a distinct bluish cast and a dirtier colour impression compared to the red pigments I, II and III.

- For iron oxide yellow pigments, as a result of these different ligand field parameters, the high-intensity absorption bands III to VI for α-FeOOH are positioned much more in the short-wave range, with the result that the rise in absorption that determines colour also undergoes a significant UV shift.

- For iron oxide orange pigments, the calculation of electron transitions I to IV provides a very good correlation with the measured band positions I to IV, as shown in Figure 7, and thus explains the colour change from yellow to orange.

- For iron oxide black pigments, at RT, the octahedrally coordinated iron ions have an average valence of +2.5, which Mössbauer spectroscopy also demonstrates with a signal split as a sextet, as the “Fe2.5+ ions” couple magnetically with the tetrahedrally coordinated iron(III) ions.

K is the absorption coefficient of the red pigment and correlates with the extinction (absorbance) E of the single crystal through the relationships

$$K = 2.302 \cdot \varepsilon \cdot d$$

and

$$E = \varepsilon \cdot d$$

With the exception of the factor 2.302, single crystal and pigment powder have comparable dependencies in terms of absorption properties.

S is a pigment’s scattering coefficient and is essentially dependent on particle size and the refractive index n.

Figure 2 shows the absorption spectrum of a red pigment with an average particle size of approximately 0.25 µm (red III). Bands I and II have virtually the same energy positions as for measurement of the single crystal, as shown in Figure 1. This is logical given the identical electron structure of the α-Fe₂O₃ materials. The correct magnitude of intensities is only obtained by measurement of the α-Fe₂O₃ single crystal.

The absorption spectrum of a saturated cadmium red pigment (Cd₅S₄Se₅, mixed phase), as shown in Figure 3, features a very steep, sudden rise in absorption that is caused by direct electron transitions from the valence
Inorganic pigments

band (VB) to the conduction band (CB). In the case of \( \alpha\)-Fe\(_{2}\)O\(_{3}\) pigments, the rise in absorption is less steep (angle of inclination \( \alpha \) at the turning point \( T_p \) is approx. 80° compared to 85° for the cadmium red pigment) and the steepness is also reduced by band II at approx. 15,500 cm\(^{-1}\). These differences lead to the \( \alpha\)-Fe\(_{2}\)O\(_{3}\) pigments being much less saturated and exhibiting much lower colour purity.

The influence of particle size on pigment colouring properties is well known. To also investigate this spectroscopically, red pigments of various particle sizes were produced using the Laux process (characterisation in line with Table 2) and investigated spectroscopically.

If considering the red pigments I to V, red III represents the reference point (average particle size approximately 0.25 µm). With increasing fineness, the colour shifts toward more yellowish products (red I and red II). When the pigment particles are increased, a significant blue shift occurs (red IV and red V).

In the transition from red III to red pigments II and I (increasing fineness), the profile of the absorption spectra is very similar (same positions for bands I and II). However, a difference exists for the intensities of band II, as decreasing particle size is accompanied by a reduction, shown in Table 2, which results in the somewhat greater colour saturation for the finer pigments. If we consider the rises in absorption, it is possible to observe a shift toward the short wave from red III to red II and red I (see inflection points in Table 2), which explains the yellow tinge of the finer red. The intensities for the finer pigments are also slightly lower than for red III.

The rises in absorption become much less intense as particle size increases, and the steepness is reduced. A slight shift toward lower wave numbers also occurs. These changes result in a distinct bluish cast and a dirtier colour impression compared to the red pigments I, II and III.

Iron oxide yellow pigments

Iron oxide yellow (goethite, \( \alpha\)-FeOOH) has the crystal structure of diaspore (\( \alpha\)-AlOOH) and contains only Fe(III) ions in an octahedral coordination. The pigments exhibit a needle-shaped habit, with a length-to-width ratio of around 5 : 1 predominating.

The smallest structural units for \( \alpha\)FeOOH are FeO\(_3\)(OH)\(_3\) octahedra, where the iron(III)-ion is coordinated asymmetrically by three oxygen (O\(^2-\)) and three hydroxyl (OH\(^-\)) ligands.

This distortion of the individual octahedra becomes clear if we look at the Fe-O and Fe-OH distances:

- Fe-O with 1 x 1.89 Å and 2 x 2.02 Å
- Fe-OH with 1 x 2.05 Å and 2 x 2.12 Å

In the crystal lattice of the goethite, these FeO\(_3\)(OH)\(_3\) octahedra form double chains through shared edges and these chains are linked to each other via corners, thus creating tunnel-like cavities [1]. There are also hydrogen bonds between the double chains, with the hydrogen atoms being located essentially in the “tunnels” of the crystal.
Absorption spectrum and colouring

At 21,500 cm⁻¹ (band III) and 24,000 cm⁻¹ (band IV), the absorption spectrum of a yellow pigment, shown in Figure 7, exhibits two intensive absorption maximums that determine colouring.

The high intensity of the two bands is due to electron transitions with particular spin-spin interactions of the five unpaired 3d electrons of two adjacent Fe(III) ions in the crystal lattice, with the rise in absorption adding additional intensity to the first electron transfer band from the O₂⁻/OH⁻ to the Fe(III) cation. A disadvantage for the saturation and colour purity of the α-FeOOH pigments is the relatively flat rise in the range from 18,500 to 20,500 cm⁻¹ (angle of inclination α at the turning point Tₚ of approx. 64°). In contrast, the rise in absorption of the brilliant cadmium yellow pigment is much steeper (angle α approx. 84°, as shown in Figure 4).

The two wide and low-intensity bands at 10,850 cm⁻¹ (I) and 15,500 cm⁻¹ (II) have no significant impact on colouring of α-FeOOH pigments.

Although the electron structures of red and yellow are very similar, a distinct short-wave shift in the rise in absorption of around 2,100 cm⁻¹ can be detected when comparing the absorption spectra, which is shown in Figure 5.

An explanation for this is provided by ligand field theory in conjunction with the structural differences of the two pigments. Fe₂O₉ double octahedra with common faces are present in the α-Fe₂O₃, while edge-sharing FeO₃(OH)₃ individual octahedra can be observed in the α-FeOOH.

In accordance with ligand field theory, the OH⁻ ion is a stronger ligand than the O²⁻ ion [3,5], with the result that a much higher ligand field strength ∆ is calculated for α-FeOOH than for α-Fe₃O₄ following evaluation of the two absorption spectra (Δα-FeOOH = 13,600 cm⁻¹ and Δα-Fe₃O₄ = 11,300 cm⁻¹). The covalence parameter B was fixed at 580 cm⁻¹ (α-Fe₂O₃) and 630 cm⁻¹ (α-FeOOH), i.e. the Fe-O bonds in the α-Fe₂O₃ exhibit higher covalence components.

As a result of these different ligand field parameters, the high-intensity absorption bands III to VI for α-FeOOH are positioned much more in the short-wave range [6], with the result that the rise in absorption that determines colour also undergoes a significant UV shift.

Iron oxide orange pigment

Lepidocrocite (γ-FeOOH) has a boehmite structure (γ-AlOOH). The smallest structural units are FeO₃(OH) individual octahedra that have three different Fe-O distances with 2 x 1.93 Å, 2 x 2.05 Å and 2 x 2.13 Å.

In the crystal lattice of the lepidocrocite, these individual octahedra form double chains through shared edges, these chains developing slightly waved layers at the b/c level of the elementary cell with further double chains. [1] The individual layers are finally bonded by means of hydrogen bonds, similar to α-FeOOH.

Light absorption and colouring

The absorption spectrum of γ-FeOOH is very similar to that of α-FeOOH, which is shown in Figure 6.
The rise in absorption for band III exhibits a steepness that is comparable with that of band III for α-FeOOH, but the position of this rise for γ-FeOOH has been shifted around 600 cm⁻¹ in the long-wave direction, shown in Figure 7, which causes the colour shift to orange. This longer-wave position of bands III and IV for γ-FeOOH can be explained using ligand field theory if the differences in the hydrogen bonds are also taken into account. In the case of γ-FeOOH, these hydrogen bonds are less pronounced due to the differing linking of the octahedron chains, so that a somewhat stronger ligand field results for the Fe(III) ions, which leads to a higher Δ value (14,000 cm⁻¹ as opposed to 13,600 cm⁻¹ for α-FeOOH). The covalence of the Fe-O bonds is comparable in the two pigments due to the calculated B values of 630 cm⁻¹. On this basis, the calculation of electron transitions I to IV provides a very good correlation with the measured band positions I to IV, as shown in Figure 7, and thus explains the colour change from yellow to orange. [6]

Causes of colouring in iron oxide black pigments

The chemical composition and distribution of Fe(II) and Fe(III) ions in the spinel lattice can be described as follows:

Fe(III)₄[Fe(II)Fe(III)]₄O₄

Ideally, the ratio of Fe(II) and Fe(III) ions to octahedron positions is 1 : 1, with the respective octahedra being linked via shared edges. At RT, the two octahedron positions cannot be distinguished, with the result that a fast electron transition from Fe(II) to Fe(III) can occur that requires only minimal excitation energies. This energy is ≥ 1,000 cm⁻¹, i.e. the entire visible light and part of the infrared light are absorbed virtually completely, thus forming the black colour of the magnetite. At RT, the octahedrally coordinated iron ions have an average valence of ≈ 2.5, which Mössbauer spectroscopy also demonstrates with a signal split as a sextet, as the “Fe²⁺⁺⁺ ions” couple magnetically with the tetrahedrally coordinated iron(III) ions. Further evidence for the indistinguishability of iron ions in octahedron positions is provided by neutron diffraction with an Fe-O distance of only 2.06 Å. [7]

REFERENCES
[2] Single crystals were prepared and measured in the working group under Prof. R. Glaum, University of Bonn, Inorganic Institute.

Table 2: Properties of α-Fe₂O₃ pigments with different particle sizes

<table>
<thead>
<tr>
<th>Product name</th>
<th>Average particle size (μm)</th>
<th>Intensity I</th>
<th>Band II Rise in absorption (cm⁻¹)</th>
<th>Intensity II Rise in absorption (cm⁻¹)</th>
<th>b⁺ (L64, pure tone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red I (yellowish cast)</td>
<td>Approx. 0.08</td>
<td>0.20</td>
<td>17,600</td>
<td>2.05</td>
<td>24.1</td>
</tr>
<tr>
<td>Red II (yellowish cast)</td>
<td>Approx. 0.15</td>
<td>0.30</td>
<td>17,300</td>
<td>2.25</td>
<td>23.7</td>
</tr>
<tr>
<td>Red III</td>
<td>Approx. 0.25</td>
<td>0.42</td>
<td>17,100</td>
<td>2.40</td>
<td>20.5</td>
</tr>
<tr>
<td>Red IV (bluish cast)</td>
<td>Approx. 0.70</td>
<td>0.50</td>
<td>16,700</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Red V (strongly bluish cast)</td>
<td>Approx. 1.0</td>
<td>0.50</td>
<td>Approx. 16,500</td>
<td>0.70</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Figure 6: Simplified electron structures of hematite and goethite

Figure 7: Absorption spectra of α-FeOOH and γ-FeOOH compared

Table 2: Properties of α-Fe₂O₃ pigments with different particle sizes