Heat-stable pigments

For surface coatings
Iron oxide pigments with improved temperature resistance for surface coating applications

The pigments of the Colortherm® and Bayferrox® T ranges have been specially modified to give them much-improved temperature resistance. They are ideal for use in coating systems, plastics and building materials where higher temperatures may occur.

Of the three most important versions of iron oxide, red iron oxides (hematite) demonstrate the highest thermodynamic stability, even at elevated temperatures. In the temperature range normally encountered in paint & coatings applications their color remains practically unchanged. Chrome oxide greens are similarly heat stable on account of their chemical structure.

In contrast, iron oxide yellow FeO(OH) (goethite) and iron oxide black Fe₃O₄ (magnetite) pigments can be converted to Fe₂O₃ (hematite) at elevated temperatures (Figure 1):

When testing the heat stability of pigments in paint & coating systems it is worth noting that the binder can have a heat stabilizing effect.

In the case of the iron oxide yellow pigments the binder delays dehydration (splitting off of water), and in the case of the iron oxide black pigments the binder slows down the reaction with oxygen.

The temperature resistance of a coating thus depends not only on the stability of the pigment itself but also on the properties of the entire coating system. To measure the pigment’s heat resistance, it is therefore essential to carry out all trials in the complete original system.

The examples in this brochure are based on a heat-stable coating system based on phenylmethylpolysiloxane formulated according to a guide formulation from Evonik Tego Chemie GmbH.

![Figure 1: The reactions of yellow- and black-iron oxides to red](image)
Iron oxide yellow
With iron oxide yellow, there is a risk of dehydration with an associated red color shift with temperatures above 180°C (Figure 2).

In the case of Colortherm® Yellow 10 and Colortherm® Yellow 20, the first option is utilized (Figure 3). By applying an additional inorganic coating to the primary particles, the surface elimination of water is delayed, consequently raising heat stability about 20°C under otherwise identical conditions (Figure 4).

The inorganic post-treatment is strongly hydrophilic, which means that wetting problems may occur with non-polar coating binders or plastics. To improve the wetting properties of

To improve the heat resistance of the yellow pigment, there are two options available:
1. Delaying dehydration
2. Converting the iron oxide yellow pigment through a chemical reaction into a new inorganic yellow pigment with higher heat stability.

Figure 2: Color change of an iron oxide yellow pigment (goethite) in a coating system based on phenylmethylpolysiloxane

Figure 3: Schematic representation of post-treatment FeO(OH)
Colortherm® Yellow 20 and avoid this problem, a process to increase its hydrophobicity is performed, in addition to the inorganic post-treatment.

With Colortherm® Yellow 3950 and Colortherm® Yellow 30, the second option (chemical reaction) is utilized. Iron oxide yellow and zinc oxide are reacted at high temperatures in a solid-state reaction to form a new chemical compound.

A synthetic zinc ferrite $\text{ZnFe}_2\text{O}_4$ is formed, which differs significantly in its heat stability from a normal iron oxide yellow (goethite). With zinc ferrite, there is no longer any risk of conversion to hematite ($\alpha\text{-Fe}_2\text{O}_3$) and the resultant red color shift.

At temperatures above approx. 250 °C, the color shade becomes a little less saturated. With Colortherm® Yellow 30 – a zinc ferrite with additional doping – this upper temperature limit is raised even further, to around 300°C (Figure 5).
It should nevertheless be kept in mind that zinc ferrites have completely different absorption behavior with regard to visible light than standard iron oxide yellows, and therefore have a color shade of their own. Colortherm® Yellow 3950 and Colortherm® Yellow 30 are light brown in full shade, whereas in reduction with TiO₂ they are reddish yellow in color.

In applications where higher demands are made on the heat stability of the pigments – for example in powder coatings or coil coatings – the yellow pigments of the Colortherm® range offer an additional advantage in terms of application reliability, because non stabilized yellow pigments are on the borderline with regard to heat stability (Figure 6).
Iron oxide black
Under oxidative conditions at temperatures above 180 °C, iron oxide black gradually converts to iron oxide red (hematite, α-Fe₂O₃). In terms of color, this chemical conversion can be identified by an increasingly brown coloration – in other words, a gradual shift towards a red color (Figure 7).

Similar to zinc ferrite, iron oxides can be converted by means of a solid-state reaction with manganese oxide into a substance that has far greater heat stability, namely manganese ferrite. Depending on the way the reaction is performed, it is possible to produce either a black (Bayferrox® 303 T) or brown manganese ferrite (Bayferrox® 645 T).

The manganese ferrites produced in this way have a heat resistance of well above 500 °C (Figure 8). Additionally, manganese ferrite differs from conventional iron oxide black pigments (magnetite) in its flocculation behavior.

In comparison to magnetite the manganese ferrites, produced via calcination, demonstrate markedly lower magnetic properties and have a flocculation stability similar to that of a normal hematite red iron oxide. In contrast to Colortherm® Yellows the manganese ferrites are also heat stable when exposed to elevated temperatures over a prolonged period of time.

Additional to the usual applications such as powder coatings and coil coatings, manganese ferrites can also be used for coatings subjected to elevated temperatures for a long period. Typical examples are coatings for exhaust pipes or ovens.
Like Bayferrox® 303 T, Bayferrox® 645 T can be used at temperatures above 500°C. Unlike regular iron oxide brown pigments, Bayferrox® 645 T is not a mixture of yellow, red and black but a single pigment. This means that separation of pigments cannot occur.

Manganese ferrite also differs from regular iron oxide black grades in its reflective behavior with infrared radiation (Figure 10). Whereas magnetite shows a high level of absorption throughout the entire wavelength range, Bayferrox® 303 T partly reflects the infrared radiation and thus does not heat up as strongly as other black surfaces.

Figure 9 shows the color change delta E* ab of a regular iron oxide black (magnetite) compared with manganese ferrite (Bayferrox® 303 T) at various temperatures in the final coating system.

Figure 10: Reflection of electromagnetic waves by Bayferrox® 318 M (magnetite) compared with Bayferrox® 303 T (manganese ferrite) as a function of wavelength

Colortherm® Yellow pigments and heat-stable brown and black Bayferrox® T grades for the surface coatings industry

<table>
<thead>
<tr>
<th>Colortherm®/Bayferrox®</th>
<th>Color</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayferrox® 105 M - 180 M</td>
<td>Red</td>
<td>α-Fe₂O₃ – fundamentally heat stable because of their structure</td>
</tr>
<tr>
<td>Colortherm® Yellow 10</td>
<td>Yellow</td>
<td>acicular iron oxide yellow (α-FeOOH) with inorganic post-treatment</td>
</tr>
<tr>
<td>Colortherm® Yellow 20</td>
<td>Yellow</td>
<td>acicular iron oxide yellow (α-FeOOH) with inorganic post-treatment plus additional hydrophobization</td>
</tr>
<tr>
<td>Colortherm® Yellow 30</td>
<td>Yellow</td>
<td>synthetic zinc ferrite ZnFe₂O₄ – fundamentally heat stable because of their spinel structure</td>
</tr>
<tr>
<td>Colortherm® Yellow 3950</td>
<td>Yellow</td>
<td>synthetic zinc ferrite ZnFe₂O₄ – fundamentally heat stable because of their spinel structure</td>
</tr>
<tr>
<td>Colortherm® Green GN-M</td>
<td>Green</td>
<td>synthetic Cr₂O₃ – fundamentally heat stable because of its structure</td>
</tr>
<tr>
<td>Bayferrox® 303 T</td>
<td>Black</td>
<td>bluish black pigment based on manganese ferrite (Fe, Mn)₂O₃ – fundamentally heat stable because of their structure</td>
</tr>
<tr>
<td>Bayferrox® 645 T</td>
<td>Brown</td>
<td>brown pigment based on manganese ferrite (Fe, Mn)₂O₃ – fundamentally heat stable because of their structure</td>
</tr>
</tbody>
</table>
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