

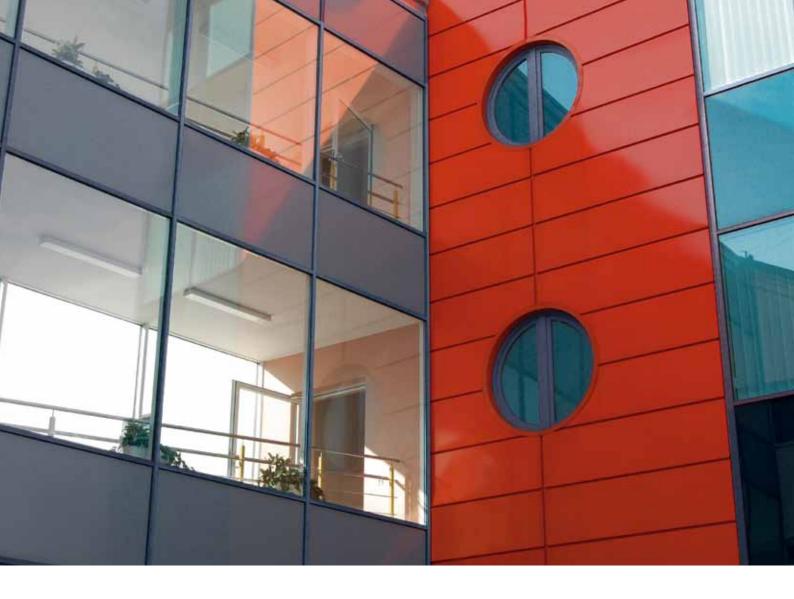




Heat-stable pigments

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 (haematites) demonstrate the highest thermodynamic stability, even at elevated temperatures. In the temperature range normally encountered in paint & coatings applications their colour 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 Fe $_3$ O $_4$ (magnetite) pigments can be converted to Fe $_2$ O $_3$ (hematite) at elevated temperatures (Figure 1):

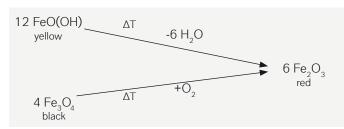


Figure 1: The reactions of yellow- and black- iron oxides to red

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



Iron oxide yellow

With iron oxide yellow, there is a risk of dehydration with an associated color shift towards red at temperatures above 180 °C (Figure 2).



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

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.

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 by around 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

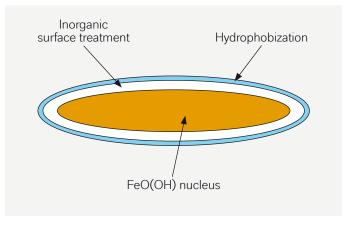


Figure 3: Schematic representation of Post-treatment FeO(OH)

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

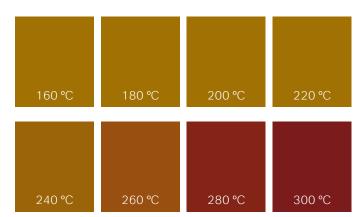


Figure 4: Color change of Colortherm® Yellow 10 in a coating system based on phenylmethylpolysiloxane at various temperatures

and zinc oxide are reacted at high temperatures in a solid-state reaction to form a new chemical compound.

A synthetic zinc ferrite $ZnFe_2O_4$ 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 (α -Fe₂O₃) and the resultant color shift to red.

At temperatures above approx. 250 °C, the shade merely becomes a little less saturated. With Colortherm® Yellow 30-a zinc ferrite with additional doping – this upper limit is raised even further, to around 300 °C (Figure 5).



It should nevertheless be borne 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 TiO_2 they are reddish yellow.

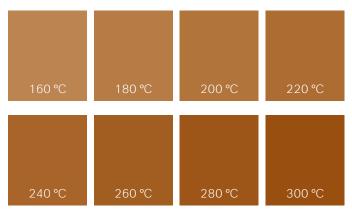


Figure 5: Color change of Colortherm® Yellow 30 in a coating system based on phenylmethylpolysiloxane at various temperatures

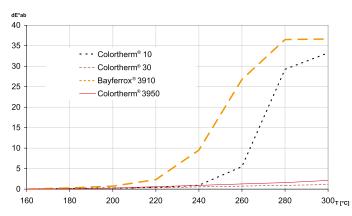
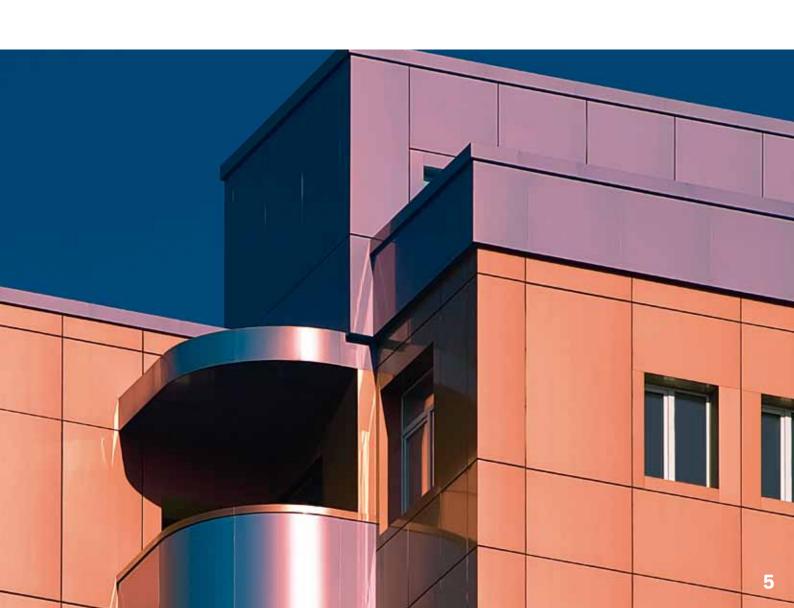


Figure 6: Color shift dE*ab of Colortherm® Yellow and Bayferrox® iron oxide yellow pigments in a coating system based on phenylmethylpolysiloxane at various temperatures

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 red (Figure 7).



Figure 7: Color change of an iron oxide black pigment (magnetite) in a coating system based on phenylmethylpolysiloxane

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 haematite 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.

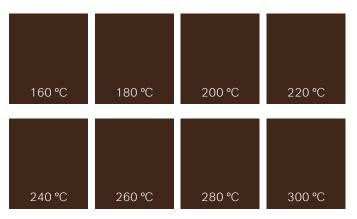


Figure 8: Color change of Bayferrox® 303 T (manganese ferrite) in a coating system based on phenylmethylpolysiloxane

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.

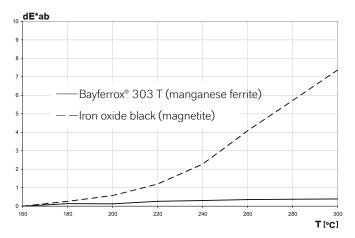


Figure 9: Color change dE*ab of Bayferrox® 303 T (manganese ferrite) and a magnetite in a coating system based on phenylmethylpolysiloxane at various temperatures

Manganese ferrite also differs from regular iron oxide black grades in its reflection 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.

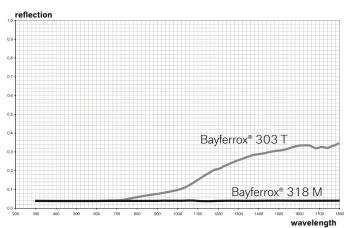


Figure 10: Reflection of electromagnetic waves by Bayferrox® 318 M (magnetite) compared with Bayferrox® 303 T (manganese ferrite) as a function of wavelength

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

Bayferrox® 105 M - 180 M	Red	α -Fe $_2$ O $_3$ – fundamentally heat stable because of their structure
Colortherm® Yellow 10	Yellow	acicular iron oxide yellow (α-FeOOH) with inorganic post-treatment
Colortherm® Yellow 20	Yellow	acicular iron oxide yellow (α-FeOOH) with inorganic post-treatment plus additional hydrophobization
Colortherm® Yellow 30	Yellow	synthetic zinc ferrite $\mathrm{ZnFe_2O_4}$ – fundamentally heat stable because of their spinel structure
Colortherm® Yellow 3950	Yellow	synthetic zinc ferrite ZnFe ₂ O ₄ – fundamentally heat stable because of their spinel structure
Colortherm® Green GN-M	Green	synthetic Cr ₂ O ₃ – fundamentally heat stable because of its structure
Bayferrox® 303 T	Black	bluish black pigment based on manganese ferrite (Fe, $Mn)_2O_3$ – fundamentally heat stable because of their structure
Bayferrox® 645 T	Brown	brown pigment based on manganese ferrite (Fe, Mn) ₂ O ₃ – fundamentally heat stable because of their structure

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