Introduction

Bright, yellow shade red iron oxides can be synthesized in a number of ways. The predominant manufacturing route is the Penniman process which is primarily used in China. The quantity of pigment produced by the Penniman process accounts for almost 1/3 of the total global market for synthetic iron oxide pigments. In the following presentation, several possible production routes are described and we will focus on a new modified version of the Penniman red process which can be used to achieve a highly saturated red iron oxide with a yellow undertone. Several options to control the Penniman production process will be discussed with the aim of reaching targeted color values. Comparisons between Penniman reds and bright, saturated reds from alternative manufacturing processes will be discussed.

Influencing factors for Penniman build up

Iron oxide red pigments are produced globally by 4 major production processes. In the "Laux Process" nitrobenzene reacts in a redox reaction with cast iron. The reaction can be controlled to produce all colors, including red. However, only the production of yellow and black Laux iron oxide pigments is used commercially. The latter is subjected to a further calcination step under oxidizing conditions to produce red iron oxide pigments. The principle raw materials for the "Precipitation Process" are iron salts, such as iron sulphate or iron chloride, derived from various sources. Precipitation is performed by adding caustic soda in the presence of air as the oxidizing agent. To ensure a uniform color development a suitable iron oxide seed is added. This technique also applies to the "Penniman Processes where steel reacts with nitric acid in the presence of air. The pigment growth is carried out by the reaction of iron with oxygen in the presence of iron nitrate. Finally, the Copperas process uses iron sulphate which is roasted under oxidizing conditions. All four processes pose specific challenges when it comes to achieving sustainable, resource-friendly production. They also have their strengths and weaknesses regarding the target color space. A new modified Penniman process is able to reach an optimum of saturation and brightness without compromising in terms of sustainability, energy efficiency or water conservation.
The Laux process offers a wide color range with particular strength in medium and bluish red color shades. The relatively hard consistency of the primary particles has its most positive effect in grades with large particle diameters. The strength of the Copperas and Penniman red grades lies in their bright, yellowish color space, which can only be achieved to a limited extent by the Laux process. Medium red tones can be obtained with both the Laux process and precipitation. The Copperas process currently offers the opportunity to prepare pigments with the highest development of bright yellow shade reds. Recent research has therefore aimed at achieving this color space by employing the Penniman process.

The Penniman Red process is made in several steps. Raw materials for this process are iron in the form of steel, nitric acid, water in the form of steam and air. To achieve defined and clean shades it is necessary to grow the particles around a defined seed. During all the production steps by-products like NOx gases or ammonium nitrate are emitted and must be taken into consideration for a sustainable process. The simplified animation shows the growing of the pigment particle. In the first step Fe$^{2+}$ adsors on the seed surface under the regeneration of nitric acid followed by the oxidation with oxygen. The generated nitric acid attacks the
iron and NO gas and NH₄⁺ is formed. The Fe²⁺ is adsorbed at the surface and the cycle starts again. The formation of NO and NO₂ is detectable as brownish gas. Our development work surprisingly revealed that, in addition to the known nitrogen oxide emissions, significant quantities of laughing gas (nitrous oxide, N₂O) are formed. Nitrous oxide is an extremely critical greenhouse gas – 300 times more potent in its effects than carbon dioxide, which already enjoys notoriety.

Iron Oxides made via the Penniman process: Growing up from seed

Looking at the color properties of bright yellowish iron oxide reds made by the Penniman process in China, it is possible to draw conclusions about the pigment build-up curve. The displayed Penniman grades are all on a similar build up curve. The yellow points and the red triangles represent the color properties of various crude iron oxides before processing. For color determination the materials have been milled on a laboratory scale. It is clear that in both full shade and reduction the red component (a*) and the yellow component (b*) do not reach the color space of a red iron oxide pigment made by the Copperas process which is shown as black square in the graph. We have intensively analyzed many different commercially available samples from the red market to learn more about the limitations of the process. After analyzing these Penniman red products, we developed ideas on how to extend the typical Penniman Red color space. After extensive research and more than 1000 Penniman red trials we were able gain a very deep understanding of the process, the mechanism and how to control the typical color development curve of the process.
Through the experience gained from the various Penniman pre-trials we succeeded in the determination of the influencing factors which have a direct effect on the pigment build up. In the case of bright yellow shade red iron oxide pigments it is thus possible to widen the color development curve to reach higher \( a^* \) and \( b^* \) color values. Furthermore, through specific measures, the build up curve can be precisely stopped at the desired color shade to enable a number of targeted color spaces to be achieved.

The influencing factors are complex and need to be applied in the right way and at the right dosage. Raw material selection and the seed quality is of fundamental importance. Besides that, the control of the reaction progress and the reaction conditions must be coordinated. No single factor is decisive, a combination of different factors will result in the highest pigment quality.
Narrow particle size distribution typically leads to a color development curve which reaches higher a* values. A precondition for this is a well-controlled pigment growth which significantly increase the brightness and chromaticity.

For color development curve with higher chromaticity particles appear more even

Coloristic of New Red Pigments

For the evaluation of pigment performance in paints and coatings, bright yellow shade iron oxide reds from various manufacturing processes were selected. The representative sample from the New Red Penniman process was designated as "Pigment 6 New Red". Two commercially available pigments from the Penniman Process were also used. In the above table the color properties in a mid-oil alkyd with "Pigment 1 Copperas" as reference are displayed.
In both full shade and reduction (1 : 5 with TiO₂) "Pigment 6 New Red" shows the highest red values (a*). It is noticeable that pigments from the different manufacturing processes do not show consistent red values (a*) in full shade and reduction. High red values in full shade often give low values in reduction and vice versa.

The differences on the b* axis are even more pronounced. The illustration shows "Pigment 6 New Red" as reference. In both full shade and reduction, all other pigments tested showed a significant shift towards blue. In reduction the level was up to 5 units.
"Pigment 6 New Red" with outstanding yellowish cast in reduction compared to bright red pigments from the market

The draw down comparison of "Pigment 6 New Red" and "Pigment 1 Copperas" in a mid-oil alkyd system shows the outstanding performance of pigments made by the new Penniman technology. Taking "Pigment 1 Copperas" as reference, the yellow component (b*) in full shade is higher by 1 unit for "Pigment 6 New Red" whereas the red component (a*) remains unchanged. Additionally a slightly lighter appearance develops.

In reduction, the drift towards a more yellow cast with respect to "Pigment 6 New Red" is more pronounced. The yellow component (b*) increases by 5 units. Coupled with an increase of the red component (a*) by approx. 1 unit "Pigment 6 New Red" surpasses the color properties of all current Penniman and Copperas iron oxide pigments available in the market.

The extraordinary color development can be predicted by just looking at the pure pigment powder. On the left side "Pigment 6 New Red" made using the new modified Penniman process is shown. The right side shows Pigment 1 made by the Copperas process.

New Red Pigments with outstanding chromaclty superior to existing
Iron Oxide Red pigments market assessable
The diverging color spaces are due, among other things, to differences in the particle morphology and particle size distribution. The exact color parameters cannot, however, be predicted using a direct correlation with the particle morphology or particle size distribution. Light, yellowish red pigments tend to exhibit a smaller particle size and an especially narrow particle size distribution, while darker red pigments are significantly larger. Due to light scattering, the size of the primary particles exert an influence on the chromaticity, tinting strength and opacity. The interaction of visible light in the wavelength range from 380 to 780 nm and particles reaches an optimum if the particles are in the magnitude of half the wavelength of the absorbed light. In the case of red iron oxide pigments, this optimum is at a particle size of 250 to 300 nm. Above and below this level, tinting strength and hiding power drop significantly. “Pigment 6 New Red” contains a high amount a fine particles in the optimum particle size range. The determination of the particle size distribution by means of the laser diffraction method is an indirect method that calculates the values from a formula that contains, among other things, the complex refractive index for hematite. The refractive index is not yet sufficiently defined and distinctive. Therefore, the values should be interpreted only comparatively. The measurement is related to the particle volume, i.e. larger particles are represented disproportionally.

**Characterization of New Red Pigments**

Another important feature for the characterization of iron oxides is their ability to be incorporated at high loadings without affecting the viscosity course. The final system should follow an approximate Newtonian flow behavior which is an advantage in enabling greater versatility during production.

To determine viscosity, the pigments were incorporated in a universal pigment concentrate with a pigment content of 61.5%. The measurement was carried out by means of a cone/plate viscometer. “Pigment 6 New Red” shows an approximate Newtonian flow in the low shear range up to 2000 s⁻¹ whereas the “Pigment 1 Copperas” is inconsistent.
Dispersibility of a pigment in a paint system is influenced by the number of aggregates and agglomerates in the pigment and by the forces holding the larger particles together. The nature of the forces could be Van der Waals forces like in the example of carbon black, hydrogen bridges as in the case of organic pigments or electrostatic forces in the case of inorganic pigments. The forces acting between particles are larger the smaller the particles are. Dispersibility is also influenced by the forces acting on the particles caused by the dispersing equipment. These forces are defined by the type of equipment and the viscosity of the mill base. The particle size of the pigments and the forces holding the particles together are given by nature. But the number of aggregates can be influenced by the pigment manufacturer by the intensity of milling. The quality of dispersion can be clearly illustrated by a photographic means. The white dots on the grinding gauge images represent protruding particles after 15 minutes dispersing with a high speed dissolver. The scaling ranges from 0 to 100 µm.

The grind values of "Pigment 6 New Red" lie in the same dimension as "Pigment 5 Laux". All other tested pigments showed an increased particle occurrence in the range 40 - 80 µm.

Easy dispersibility by using New Reds from the modified Penniman process
Conclusion

With the new Penniman technology we succeeded in reaching highest saturation ever seen for iron oxide red pigments.

All this is made possible by discovering the major influencing factors for the Penniman reaction. The New Red types are characterized through:

- Surpassing levels of red (a*) and yellow (b*) component
- Excellent performance in paints and coatings systems
- Uniform shaped particles
- Very narrow particle size distribution