Coloured titanium pigments for high performance systems. Yvonne Brussaard, Birgit Genn.

A new class of high performance of yellow, orange and red pigments are titanium based colourants. They exhibit maximum gloss, opacity, strength and durability, which cannot be achieved with today's well established blends between organic HPPs (High Performance Pigments) and white or yellow titanium or bismuth vanadate pigments.

In the past chrome and cadmium pigments were the preferred choice for opaque and full shade coatings that call for brilliant colours of yellows, oranges, reds, browns and greens. Since the ban of these pigments [1], formulators had to choose between several alternative non-toxic options. Five working off these challenges, "Ticos" titanium based light organic colour components and consequently the pigments were born.

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Challenges are needed
The deficiencies that were necessary to be overcome can be summarized as follows:
- avoid the whitening effect of titanium white
- avoid the photocatalytic (burning glass) effect of titanium white
- improve the colour cleanliness of titanate carrier pigments
- improve the gloss of titanate carrier pigments
- reduce the high abrasiveness and improve shear stability of final colour
- improve the opacity and strength of titanate carrier pigments
- avoid the separation between the heavy inorganic and the light organic colour components and consequently the floating, metamerism and insufficient colour development.

By working off these challenges, "Ticos" titanium based pigments and in the following text called new titanium based pigments were born.

Solution: bonding instead of blending
An essential task of this R&D challenge was the search for titanium carrier pigments, which combine lower abrasiveness with optimal gloss, opacity, chroma and UV-protection. As a second building block a process for a special pre-treatment of high performance organic colour pigments had to be found that would allow this component to attach easily to the inorganic carrier by a novel bonding technique. A firm link such as the one created by this bonding technique is needed before the two pigment components can perform like one. This contributes considerable value in use with respect to colour saturation, gloss, opacity, strength and stability and allows to produce shear stable final colours. The new titanium based pigments offer a better cost to performance ratio than any of the traditional options. The performance of these new titanium colours is summarised below.

Maximum opacity with full colour saturation
The unique effect of the bonding technology on colour saturation is illustrated in Figure 1. The new titanium based pigments achieve identical saturation at only 38% PY 151 loading as compared to 67% for blends between titanium white with PY 151. It is obvious that a 67% loading of organic pigment in such blends leaves too little space for gaining sufficient opacity from the titanium component. The reverse is true for the new titanium based pigments, which allow high loadings for the new titanate carrier pigment without compromising full colour saturation. This explains, why the new titanium based pigments combine maximum opacity with full colour saturation.

Fastness properties are improved
A further benefit of the new titanium based pigments bonding technology is a significant improvement in light and weather fastness. As opposed to titanium dioxide, which has been known to exhibit photocatalytic activity [3, 4] accounting for weather induced degradation mechanisms, the new titanium carrier pigments of "Tico" act like UV absorbers and protect the sensitive organic pigment from UV-attacks in a similar fashion through which sunglasses protect our eyes.

Figure 2 illustrates the improved durability of the new titanium based pigments in contrast to the hidden costs imposed by the destructive effect of titanium dioxide on the light and weather fastness of the highly valuable organic high performance pigment.

Note the fact that the weather resistance of TiO₂ /PY 151 blends falls within a comparable range with highly stabilized chromate and bismuth vanadate pigments, whereas "Tico Yellow 594" (also based on PY 151) sets new standards for durability, which up to date are not available from other highly saturated and opaque colour options.

Figure 2: Accelerated weathering in a water born styrene acrylic resin in accordance with DIN EN ISO 11341-1-A, 1998, comparing the performance of PY 151 based "Tico Yellow 594" with a blend of PY 151 with titanium dioxide and stabilised chromate and bismuth vanadate pigments.

Shorter grinding times
High performance organic colourants and inorganic pigments differ significantly with respect to their surface characteristics and their specific weights. This is the underlying reason, why inorganic pigments incorporate much easier into coating systems than their organic counterparts.
counterparts. The difference in dispersion properties becomes even more problematic, when blends between inorganic and organic pigments are incorporated into coating systems as shown in Figure 3 below. The new bonding technology resolves this problem by preparing a pre-dispersed form of the two pigment, which allows significantly shorter grinding times comparable to those for pure inorganic pigments (Figure 3).

Figure 3: Dispensibility for "Tico Red 655" vs. a regular blend resp. the pure organic pigment in a solvent based alkyl resin, using a ball mill with 2mm glass beads. A fineness of grind of 5µm is set as a quality target for high performance applications.

Dusting is reduced

The new bonding-technology offers two further advantages compared with straight blends:
- The oil absorption can be greatly decreased, allowing for higher pigment loadings in colourfast pastes,
- The tendency for dusting is significantly reduced (Figure 4).

Figure 4: The new titanium based pigments products offer approx. 10fold reduction in the lung respirative fine dust particle concentration compared to handling the tested organic pigments (acc. to DIN 55992-1 in a Heubach dustmeter type 1).

Universal use

The new titanium based pigments qualify for the requirements of nearly all demanding applications in the coatings and plastic industry such as:
- OEM and automotive refinish coatings
- Industrial coatings
- Architectural coatings
- Exterior decorative coatings
- Powder coatings
- Marine coatings
- Can coatings
- Plastic applications for PVC, PE, Polyolefins and engineering plastics.

Their use is recommended for coatings and plastics requiring high colour saturation and good hiding power at the same time.

Formulation costs

Looking at the properties of the new titanium based pigments raises the question for the price and the value, at which these new colourants come to the market. The answer is summarized in the Tables 1 and 2, showing the relative formulation costs of alternative pigmentation at equal opacity for two typical brilliant RAL-colours, i.e. Flame Red (RAL 3000) and Traffic Yellow (RAL 1023). As expected, these new pigments do not match the cost of chromate pigments, but offer both, a lower cost alternative and also higher performance than the other lead and chrome-free options available for achieving RAL-colours. These pigments are non-toxic and environmentally friendly alternatives to cadmium and lead containing pigments, and match the following EU-regulations:
- They are non hazardous under Council Directives 67/548/EEC and 1999/45/EC and latest amendments as well as their national implementations.
- These pigments need not to be classified as "hazardous waste".
- They comply with the purity requirements of EN 71-3:1994 for safety of toys.

Literature


Result at a glance

- "Ticos" show best fastness properties compared to blends between HPP organics/TiO2, bismuth vanadates and lead chromate/molybdate pigments.
- They are highly opaque and sufficiently saturated to cover important full shade industry colours like e.g. defined in the RAL register, but also branded shades like Coca Cola Red, Shell Yellow or John Deere Green.
- The processing and handling characteristics are superior to those of typical organic colourants and provide easy dispersibility combined with low dusting properties.
- These pigments are recommended for opaque and brilliant full shade or close to full shade applications, which demand high performance characteristics.
- Formulation costs with theses new pigments are lower if compared to alternative high performance colour solutions.

Options for lead chrome replacement

1. HPPs (High Performance organic Pigments) fulfill most of the quality requirements, especially since more and more opaque HPPs have become available, which combine very clean shades of yellows, oranges and reds combined with excellent fastness properties. The drawback are the high costs of HPPs, which are up to 20 times higher then those for chromate pigments.

2. Bismuth vanadates appear as a second alternative, but can not always satisfy stability and cost requirements for specific applications.

3. Iron Oxides can be used in general applications as long as dull colours and the overall properties of iron oxides can be tolerated.

4. Blends between HPPs and titanium dioxides are more economical, but have the disadvantage of whitening the original brilliant chroma of the HPPs. Furthermore, the presence of titanium dioxide leads often to photocatalytic reactions on exposure to UV light and impacts on the fastness properties of the organic HPP pigment ("burning-glass effect"). While the light fastness of most HPP organic colours in pure tone applications reaches the top rating of "8" by the wool scale, the photocatalytic attack caused by titanium dioxide reduces these excellent fastness properties by 1, 2 and in extreme cases by 3 units, and this way takes away much of the benefits of these highly valuable pigments.

5. Blends between HPPs and titinate yellows overcome this problem in theory, but so far it had not been possible to fully exploit the natural synergy between these two pigment classes by combining them through dry and wet blending technologies. The opacity, colour strength and chroma achieved by these techniques is insufficient. In some cases, the high abrasion, particularly of nickel titanates, prevents the development of a shear stable colour. These disadvantages account for much of the limited use, rutile yellows have seen so far.

6. "Tico", the new titanium based pigment, prepared by "bonding" organic colourants to the surface of titinate carrier pigments. As a result they develop full colour saturation and high gloss, low dusting properties and are easy to disperse. The valuable organic pigments are protected by the "sunglass effect" of specially designed titinate carrier pigments, which leads to outstanding light and weather fastness.
The authors:

-> Yvonne Brussaard studied chemistry in Hamburg/Germany and received her Ph.D in organometallic chemistry from the Technical University of Clausthal/Germany in 1998. She joined Heubach GmbH as an R&D specialist for inorganic color pigments. Since 2001, she has been responsible for the development, production and market introduction of the “Tico” product line.

-> Birgit Genn studied chemistry at Fachhochschule Aachen. After working for Bayer Polymers in development and technical marketing of coatings in Leverkusen/Germany and in Shanghai/China, she joined Heubach GmbH in 2003 as Technical and Marketing Development Manager Americas and is now responsible as Head of Business Unit Mixed Metal Oxides.
Figure 1: Example showing the development in color saturation for "Ticos" with bonded P.Y. 151 compared to a blend of titanium white with PY 151. Application at 10% pigmentation in a solvent based alkyd resin.
Figure 2: Accelerated weathering in a water born styrene acrylic resin

Accelerated weathering results
styrene acrylic resin 12% pigmentation

- **Tico Y 594**
- Bismuth vanadate
- stab. lead chromate
- standard lead chromate
- P.Y. 151 / TiO₂

DE
5
4
3
2
1
0

hours in Xenotest
Figure 3: Dispersibility for "Tico Red 655" vs. a regular blend resp. the pure organic pigment in a solvent based alkyd resin.
Figure 4: The new titanium based pigments products offer approx. 10fold reduction in the lung respirative fine dust
### Table 1: Cost Comparison at equal opacity of Flame Red RAL 3000

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>C.I.</th>
<th>Lead</th>
<th>&quot;Tico&quot;</th>
<th>Vanadate</th>
<th>Organic</th>
</tr>
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<tbody>
<tr>
<td>Molybdate Red</td>
<td>P.R.104</td>
<td>75.9 %</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>BONA, Mn</td>
<td>P.R.52:2</td>
<td>8.2 %</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Benzimidazolon</td>
<td>P.O.36</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>51.9 %</td>
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<tr>
<td>DPP-Red</td>
<td>P.R.254</td>
<td>–</td>
<td>–</td>
<td>44.6 %</td>
<td>–</td>
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<tr>
<td>Perylene</td>
<td>P.R.178</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.7 %</td>
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<tr>
<td>Bismuth vanadate</td>
<td>P.Y.184</td>
<td>–</td>
<td>–</td>
<td>29.4 %</td>
<td>–</td>
</tr>
<tr>
<td>&quot;Tico Red 655&quot;</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>50.2 %</td>
<td>–</td>
</tr>
<tr>
<td>Chrome Titanate</td>
<td>P.Br.24</td>
<td>–</td>
<td>39.7 %</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Iron Oxide Red</td>
<td>P.R.101</td>
<td>4.5 %</td>
<td>10.1 %</td>
<td>17.4 %</td>
<td>7.0 %</td>
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<tr>
<td>Titanium dioxide</td>
<td>P.W.6</td>
<td>11.4 %</td>
<td>–</td>
<td>8.6 %</td>
<td>25.3 %</td>
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<tr>
<td>Cost ratio compared to lead chrome</td>
<td>–</td>
<td>1</td>
<td>4</td>
<td>10</td>
<td>7</td>
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</table>
### Table 2: Cost Comparison at equal opacity of Yellow RAL 1023

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<tr>
<th>Pigment type</th>
<th>C.I.</th>
<th>Lead</th>
<th>&quot;Tico&quot;</th>
<th>Vanadate</th>
<th>Organic</th>
</tr>
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<tr>
<td>Lead Chromate</td>
<td>PY.34</td>
<td>89.3 %</td>
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<td>-</td>
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<tr>
<td>Bismuth vanadate</td>
<td>PY.184</td>
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<td>-</td>
<td>79.4 %</td>
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<tr>
<td>Isoindoline</td>
<td>PY.139</td>
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<td>-</td>
<td>1.9 %</td>
<td>-</td>
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<td>Quinophthalone</td>
<td>PY.138</td>
<td>-</td>
<td>-</td>
<td>18.7 %</td>
<td>-</td>
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<tr>
<td>Benzimidazolon</td>
<td>PY.151</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>75.4 %</td>
</tr>
<tr>
<td>&quot;Tico Yellow 594&quot;</td>
<td>-</td>
<td>-</td>
<td>68.4 %</td>
<td>-</td>
<td>-</td>
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<tr>
<td>&quot;Tico Yellow 622&quot;</td>
<td>-</td>
<td>-</td>
<td>3.1 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel Titanate</td>
<td>PY.53</td>
<td>-</td>
<td>28.5 %</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Chrome Titanate</td>
<td>P. Br. 24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.5 %</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>P.W.6</td>
<td>10.7 %</td>
<td>-</td>
<td>8.1 %</td>
<td>-</td>
</tr>
<tr>
<td>Cost ratio compared to lead chrome</td>
<td>-</td>
<td>1</td>
<td>7</td>
<td>8</td>
<td>10</td>
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