Effects without Drawbacks

Special Encapsulation Makes Metallic Effects Inert and Weather-Resistant

Pearlescent pigments produce striking effects in thermoplastics. However, the natural photoactivity of TiO_2 influences the stability of the polymer matrix. Unlike off-the-shelf organic stabilizations, the inorganic "Way" technology significantly reduces the photoactivity of effect pigments, which in turn opens up new design possibilities for plastic products with high UV exposure.

Whether in automobiles, consumer goods or mobile devices, metallic luster is in demand. Organic-coated TiO_2 pearlescent pigments have been established in coating systems for many years. Now the trend leans toward mass-dyed plastic components that include new stabilizing additives (© stock.adobe.com/Surrender)

Choosing a plastic for a particular application often requires one to review countless data sheets and articles. The plastic must be subsequently altered with additives such as light stabilizers, impact modifiers and antioxidants. After this time-consuming process, why would anyone add a colorant that could negatively affect the properties of the plastic/additive system or even cause inadequate chemical stability or lightfastness in the system, which has been so carefully considered? Of course, one would like to prevent this, but the influence of a colorant on a finely tuned system is too often overlooked. Any colorant that is added to a complex system of plastic and additives must be as inert as possible in order not to create an interaction with undesirable consequences.

Metallic Effects with Pigments of High Stability

There are two possible types of additives for mass-dyed molded parts to create the metallic effects sought after by the »

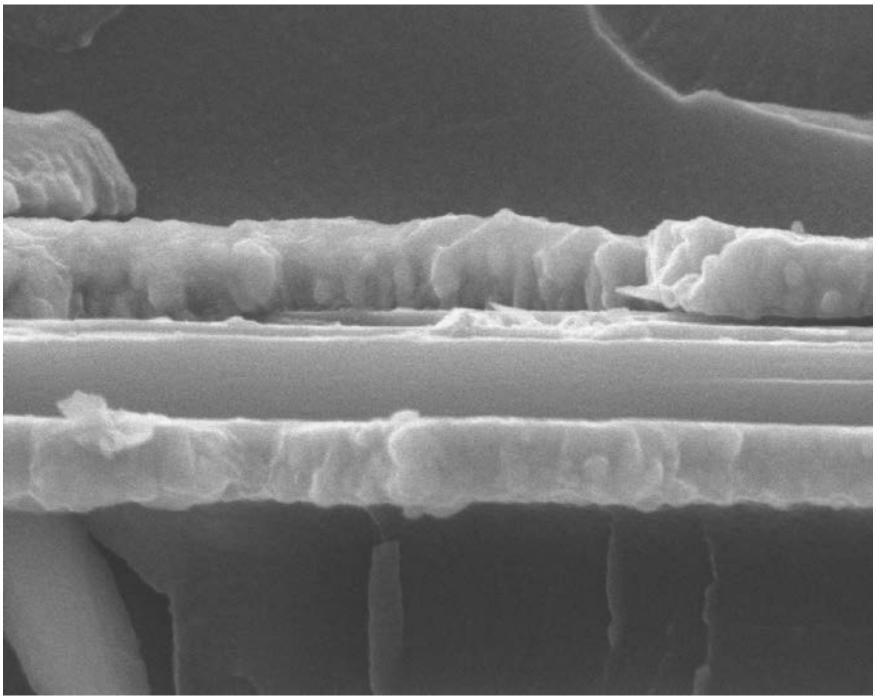

Fig. 1. Scanning electron microscope (SEM) image of a TiO_2-based pearlescent pigment (© Merck KGaA Darmstadt)

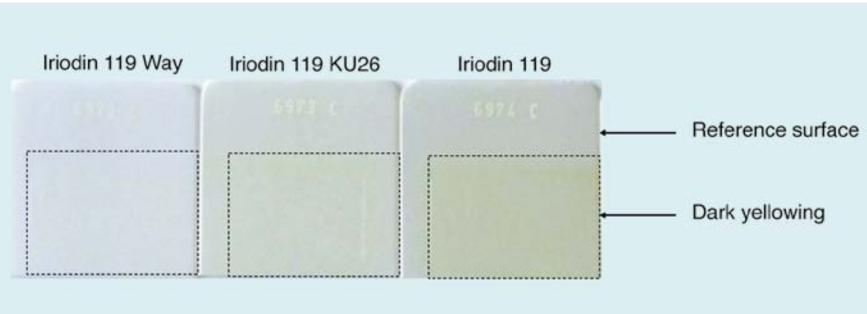

Fig. 2. Comparative tests on dark yellowing with different types of encapsulation. Unlike the standard pigment on the right, Iriodin 119 Way shows no yellowing after 284 h of exposure to UV radiation (© Merck KGaA Darmstadt)

automotive, electronics, consumer goods industries and other markets: metal effect pigments or layer-substrate effect pigments. In the past, the metal effect pigment industry developed a multitude of modifications of metallic pigments that reduce interactions between the metallic pigments and the plastic/additive system. Some modifications work better than others, but metal effect pigments have one major drawback: limited coloring possibilities in combination with other colorants owing to the metal particle's inherently opaque color. Effect pigments based on layer-substrate particles are well known for their "pearlescent effect," and allow one to formulate a much broader color spectrum than with metal effect pigments.

Figure 1 shows a classic scanning electron microscope (SEM) image of a TiO_2-based effect pigment. The layer-substrate combination is essential to the effect of each effect pigment; shown here is mica with a TiO_2 layer. Over many years, the development promoted by the automotive industry has resulted in organic-coated versions with improved weather and light resistance in paint systems. Now the trend is advancing, and painted components, for example for the automotive industry, are being replaced with paint-free, mass-dyed plastic components. This saves weight and reduces fuel consumption. In addition, the energy-intensive drying of the paint during the components manufacturing is eliminated and thus the CO_2 balance is improved. However, the weather and light resistance of these pigments must fulfill the same criteria as for paint finishes.

The organic-coated metal effect pigment versions cannot be used effectively in thermoplastics because the organic coating has poor heat resistance at process temperatures above 200 °C. Similarly, the organic coating prevents very inadequately thermal or photochemical reactions that also might occur. Effect pigments that can withstand temperatures used in processing plastics are normally photocatalytically active and therefore react with the entire system in which they are incorporated. For any colorant, particularly for metal oxide layer-substrate pigments, it is especially demanding to be weather-, light- and heat-resistant as well as chemically and photochemically inert. That is why Merck KGaA, Darmstadt, Germany, has developed the Way technology. By applying an inorganic, ceramic-like encapsulation on the pigment surface, it has become possible to provide a colorant that barely reacts in the added system. It can be mixed into a finalized plastic/additive system formulation without subsequent undesirable photocatalytic reactions.

Temperature-Stable Pigment Encapsulation for High Resistance

Way is an acronym for "weathering and anti-yellowing." While "yellowing" often can be attributed to aging and weathering, in the case of titanium dioxide-coated layer-substrate effect pigments, it is also a chemical reaction between the chemically active surface of these effect pigment types and phenolic groups. This reaction causes yellowing and occurs in the absence of light. Therefore, this phenomenon is known as "dark yellowing." Although surface-treated pigment types to reduce this phenomenon are available from a number of manufacturers, their functionality varies from being virtually ineffective to significantly suppressing dark yellowing, as in the case of the surface-modified KU26-grade Iriodin pigments and KU28-grade Miraval pigments.

The dark yellowing effect is caused by hydroxyl groups on the surface of the pigment, which in the absence of light, react with certain phenolic compounds that are contained in many antioxidants. These functional OH groups emerge

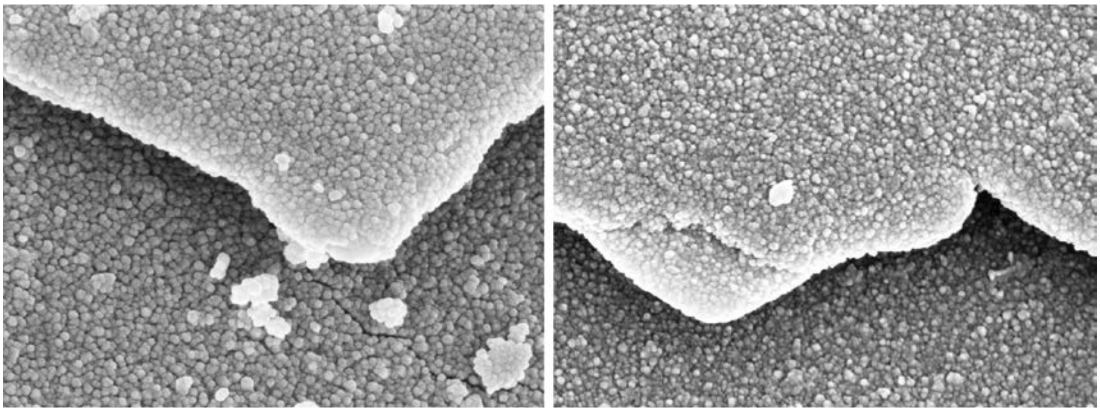

Fig. 3. SEM image of pearlescent pigments Iriodin 103 (left) and Iriodin 103 Way (right). The new stabilization does not disturb the visual properties of the pigment (© Merck KGaA Darmstadt)

during the manufacturing process, and depending on the manufacturer, can appear from a minimal to a significant degree. The larger the number of these OH groups, the more susceptible the pigment is to dark yellowing. Higher requirements on the quality of pigments necessitate a lower emergence of such hydroxyl groups. However, these OH groups cannot be completely avoided, and even with the industry-leading KU26 and KU28 grades, dark yellowing may still occur under extreme circumstances, for example when the packaged product has a high butylhydroxytoluene (BHT) content.

In order to avoid this phenomenon as much as possible, the pigment is encapsulated in the Way stabilization, so that the surface-active OH groups no longer come into contact with phenols and thus any reaction is prevented. **Figure 2** shows the different degrees of yellowing, depending on the type of encapsulation. Comparative tests of a standard pigment, a KU26-grade pigment and a Way-stabilized pigment in the presence of BHT show absolutely no dark yellowing of the Way-stabilized pigment (left), reduced dark yellowing of the KU26-grade pigment (center) and significant dark yellowing of the standard pigment (right), following exposure to UV radiation in the presence of moisture.

Full Effect due to Robust Stabilization

Another aspect of yellowing triggered by TiO_2-containing effect pigments is the oxidative degradation through UV radiation of the plastic and the additives contained therein. TiO_2 is inherently photocatalytically active and, if exposed to UV radiation, can cause yellowing and alteration of physical properties, including potential premature product failure, in a wide range of plastics. The titanium dioxide pigment manufacturers have a broad spectrum of treated and coated variants that exhibit high lightfastness and chemical resistance. Almost all of these systems used by the TiO_2 pigment industry cannot be used for layer-substrate effect pigments because they adversely affect the refractive index of the layer and thus the color and effect.

According to the current state of technology, only organic coatings can be used. However, they do not withstand standard temperatures during the processing of thermoplastics. Way stabilization was developed for pearlescent effect pigments to achieve an equal or better lightfastness and chemical resistance than with high-resistant TiO_2 pigments. In doing so, the pearlescent effect ought to be retained and the coating should be resistant to high temperatures. Way stabilization is suitable for all plastics and applications. Even under the microscope, »

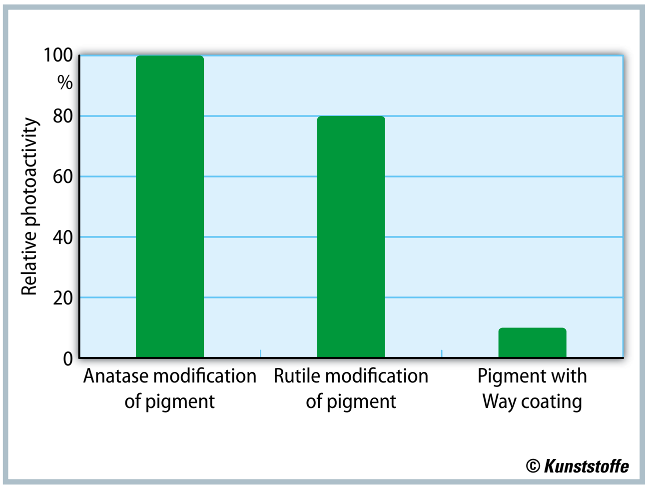

Fig. 4. Relative photoactivity of different types of encapsulation, which has a direct impact on the overall system's light resistance and is lowest with the pigment with Way coating (source: Merck KGaA Darmstadt)

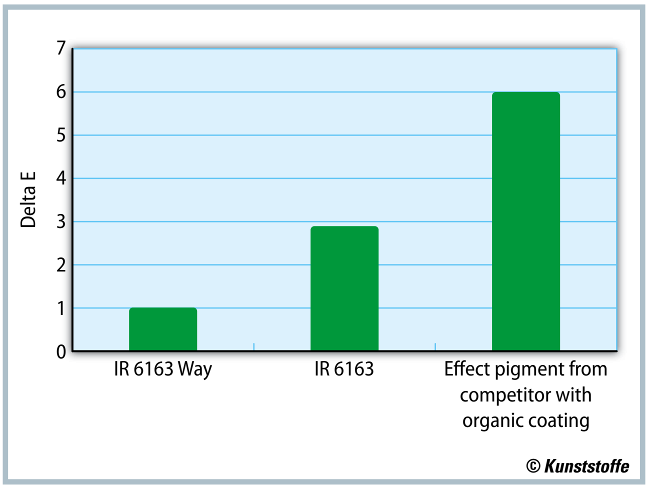

Fig. 5. Color change Delta E: Iriodin 6163 Way compared to Iriodin 6163 and a competitor's pearlescent pigment with organic coating, each with 1 % in PMMA after 5000 h in the sun tester according to DIN EN ISO 11341 (source: Merck KGaA Darmstadt)

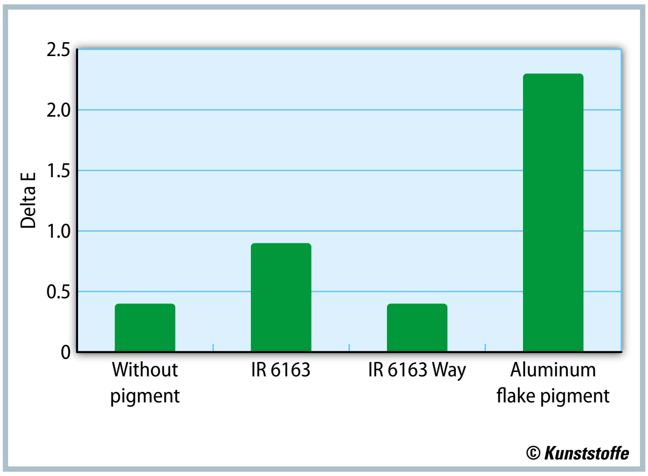

Fig. 6. Delta E color change of various pigments with 1% in PP, immersed for 35 days in 5% ammonia solution (source: Merck KGaA Darmstadt)

there is almost no difference in the effect between the Way version of an effect pigment and its non-Way variant (**Fig. 3**).

Proven Functionality and Color Stability

Way stabilization ensures that the visual metallic effect remains. The secret lies between the layers and is therefore difficult to recognize. The consequence is that the previously known photoactivity of TiO_2-based effect pigments is almost completely eliminated. **Figure 4** illustrates the relative photocatalytic activity of a Way-coated pearlescent pigment compared to an anatase- and a rutile-TiO_2-coated effect pigment. This photocatalytic activity is related directly to the light resistance of the overall system. It can affect the plastic and any additives possibly used. Also observed were interactions with light stabilizers whose effectiveness became reduced through the photocatalytic activity. If effect pigments without Way stabilization are used, the carefully tuned polymer/additive formulation may lose its balance and affect the long-term stability of the mechanical properties.

Deformation	IR 6163 Way	Aluminum pigment
Permanent	7.07 mm	16.41 mm
Elastic	18.94 mm	17.91 mm
Total	26.01 mm	34.31 mm

Table 1. Result of a micromechanical scratch test to quantify the deformation when using 1% Iriodin 6163 Way or 1% aluminum pigment in PP. Conditions: 1000 h in the sun tester according to DIN EN ISO 11341 (source: Materials Testing Laboratory of Darmstadt University of Applied Sciences)

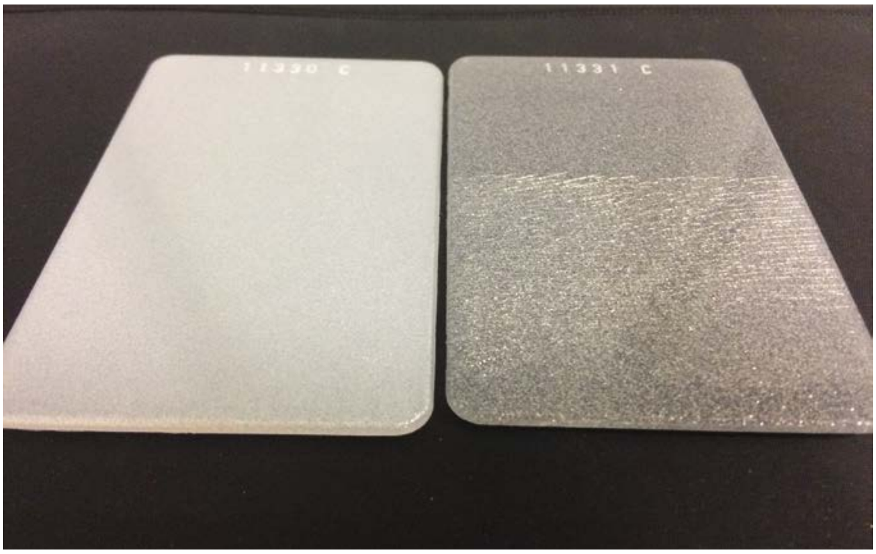

Fig. 7. Microscopic cracks after 400 h in the sun tester according to DIN EN ISO 11341 of Iriodin 6163 Way (left) and aluminum flake pigment (right) with 1% in PP (© Merck KGaA Darmstadt)

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Pigment type	Aluminum pigment	Way effect pigment
Drop height in [m] of a 1 kg weight	0.03	0.5
Drop speed at impact [m/s]	0.77	3.13
Resulting energy [J]	0.29	4.90

Table 2. Results of a drop test to determine the mechanical stability (drop height to material fracture). Two different PP specimens, respectively with 1% Iriodin 6163 Way or 1% aluminum pigment were compared after six months of outdoor weathering (source: Materials Testing Laboratory of Darmstadt University of Applied Sciences)

Tests comparing Way and a corresponding untreated pigment with a competitive product show significant differences in lightfastness with regard to color changes (Delta E). The test shown in **Figure 5** was carried out for 5000 h on samples with 1% pigment in polymethylmethacrylate (PMMA) according to DIN EN ISO 11341. Way stabilization does not only reduce interactions in the compound system and thus improves light- and colorfastness, it also demonstrates excellent chemical resistance. In many applications, contact with reactive materials may occur. Harmful vehicle emissions contain many reactive substances that can have a devastating effect on plastic components in their environment. Way stabilization makes the whole system resistant to these harmful substances and helps maintain color and physical properties.

Chemically Durably Stable

In order to predict chemical resistance, polypropylene formulations containing a Way pigment, a non-Way pigment, and aluminum, respectively, were immersed in ammonia solution and their Delta E color change was measured (**Fig. 6**). Even in comparison with other methods for producing metallic effects, Way shows advantages in terms of colorfastness, chemical resistance and inhibited interactions with the overall system, and enables a wide spectrum of colors.

Identifying and qualifying surface changes after long-term use of plastics is an important quality criterion. In this case, surface damage assessment was conducted visually and micromechanically using a UST (universal surface tester, manufacturer: Innowep GmbH, Wuerzburg, Germany). The results of the micromechanical scratch resistance tests (**Table 1**) confirm the visual differences (**Fig. 7**) between two identical formulations of Way and aluminum in polypropylene copolymer following exposure to UV radiation. The Way pigment sample exhibits less damage of physical properties than the aluminum pigment.

Compared with aluminum pigments, the overall mechanical stability of a plastic component after weathering is significantly better when using Way pigments. A drop test developed by the Materials Testing Laboratory of Darmstadt University of Applied Sciences, Germany, was employed (**Fig. 8**). Evaluated were two different samples made of PP, each with 1% of a Way effect pigment or an aluminum pigment. The drop tests were carried out after the samples were exposed to outdoor weathering for six months. The sample colored with 1% of a Way pigment shows a tenfold higher stability than the same sample colored with 1% of an aluminum pigment (**Table 2**).

Fig. 8. Set-up of a drop test to determine the mechanical stability when using 1% Iriodin 6163 Way or 1% aluminum pigment in PP (© Materials Testing Laboratory of Darmstadt University of Applied Sciences)

Conclusion

Way stabilization enables metallic effects in a great variety of plastics for applications that must withstand extreme environmental conditions. Compared to normal metal effect pigments, it exhibits minimal reactivity with the system and achieves improved long-term stability, both in terms of color and physical properties. The thermal resistance of the Way stabilization allows it to be used in all thermoplastics, and here too guarantees lasting stabilization. ■