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SPARKLING RESULTS WITH SPACER TECHNOLOGY

A new class of pearlescent pigments offers significant improvements in colour intensity, sparkle, and lustre. By Michael Gruener, Thomas Schneider, Ralph Schneider, and Guenter Kaupp, Eckart.

Pearlescent pigments have a long history in the effect pigments market and are well established in coatings, graphic arts, plastics, and cosmetics applications. An overview can be found in "Special Effect Pigments" by G. Pfaff [1].

Conventional pearlescent pigments consist of a transparent platelet-like substrate, preferably of low refractive index, which is coated with a minimum of one high-refractive-index material. Typical low-refractive substrates are mica, synthetic mica, alumina, glass, silica, and the like. Corresponding high-refractive materials for the surrounding coating are titanium dioxide, iron oxides, tin oxide, and mixtures thereof [2]. This coating, too, can comprise several alternating layers of high- and low-refractive materials, with, for example, alumina, silica, or silica modifications serving as low-refractive intermediate layers [3]. Multilayer pearlescent pigments can provide attractive and improved colour properties, compared with single-layer-type products, but their performance in terms of colour, effect and chemical stability is sometimes limited.

STRUCTURAL SPACER ELEMENT VERIFIED BY SEM AND STEM ANALYSES

A brand-new type in the world of pearlescent effect pigments is that of spacer products. These have a similar composition to conventional pearlescent pigments in that they comprise a transparent platelet-like substrate of low refractive index and are coated with high-refractive metal oxides.

However, these pearlescent pigments possess a unique structural element which can be described as a layer of periodic-like nano cavities, called a spacer (see *Figure 1*).

Examples of such pearlescent pigments comprising these structural spacer elements are shown in the SEM cross-section images in *Figure 2*, where the periodic-like nano cavities can easily be identified.

The SEM images show the intermediate cavities or spacer layer surrounding the complete pigment exactly in parallel with the substrate's surface (*Figures 2a–d*), which is ideal for oriented interaction with light to provide optimum optical performance. The cross-section shown in *Figure 2b* conveys an almost 3-dimensional impression, in which not only the layer sequence of inner metal-oxide layer, spacer and outer metal-oxide layer can be observed, but also part of the surface and surface morphology of the outer metal-oxide layer.

These nano cavities and spacer layers can range from 2 to 119 nm in height, with values typically between 18 and 53 nm, as indicated in *Figure 2d*.

Detailed SEM studies, including EDX (energy-dispersive x-ray spectroscopy) analysis along the pigment's cross-section, yielded the plots shown in *Figure 3*, which provide further evidence of the structural spacer element.

RESULTS AT A GLANCE

→ Novel class of spacer-type pearlescent pigments developed.

→ They possess a unique structural element of periodic-like nano cavities, called a spacer.

→ The spacer and its effective low refractive index play a key role in the optical performance.

→ They offer significant improvements in chroma, sparkle, lustre, and stability.

Most remarkable is the oxygen plot (blue line) for the metal oxides contained in the substrate and the metal-oxide coating surrounding it. This undergoes a substantial drop in intensity on both sides of the pigment, a fact which clearly indicates the presence of spacer layers. Also, the metal plots M1 and M2 (yellow and purple lines) display a less pronounced drop in intensity, the extent of which depends on the amount of metal oxide in the coating layers. Finally, the outline of the substrate, which in this case consists mainly of silica, is shown by the orange line. Virtually no other element is detectable in the cross-sectional area of these intensity drops. In summary, the unique structural element of the spacer unit within the regular metal-oxide coating is clearly confirmed. Similar results have also been obtained in separate STEM analyses [4].

EFFECTIVE LOW REFRACTIVE INDEX OF SPACER LAYER IS KEY

The various physical laws regarding the interaction of light with thin films are explained in detail in several articles [5].
As a rule of thumb, the greater the difference in refractive indices between the substrate and high-refractive metal oxide or the intermediate low-refractive layer and high-refractive metal oxide, the better and more intense are the optical effect and the colour impression.
The simplified reflectivity model shown in *Figure 4* demonstrates the interaction of incident light at the boundary surfaces between materials of low refractive index n_1 and high refractive index n_2. At any boundary layer, the light is split into reflected and transmitted portions. Finally, all recombined portions of reflected light R1, R2 etc. define the interference colour, whereas all recombined portions of transmitted light T1, T2 etc. add up to give the transmission colour. For every wavelength, there is an optimum condition for maximum reflection defined by the given equations, which depend only on the material constants n_1 and n_2 and the physical distance d. In other words, the optimum reflection of a specific interference colour is improved the more the refractive indices n_1 and n_2 differ from each other or the lower the refractive index n_1 is for a given n_2. Accordingly, in this effect pigment class, the spacer layer and its effective low refractive index play the key role.
In general, the structure of the spacer layer resembles a foam. Large cavities, which are almost totally devoid of solid material and are only gas-filled, are surrounded by very small walls of carrier material. The optical behaviour of this layer is therefore mostly dominated by the cavities.

GAIN IN REFLECTIVITY

Although the refractive index of nano layers cannot be measured directly, one can imagine that the refractive index of said spacer element must be quite low, as otherwise the optical performance could not be explained. Theoretical calculations indicate that the refractive index of the spacer unit is clearly below 1.3. Consequently, the reflectivity and the colour intensity are boosted significantly, because the reflective index of the internal boundaries between cavities and high-refractive material is significantly greater than that of conventional pearlescent pigments having metal oxides based on high- and low-refractive materials. For example, compared with a low-refractive SiO_2 layer, the gain in reflectivity and the advantage conferred by a spacer layer can be roughly estimated to be in the range of 10 to 30 %.

Figure 1: Comparison of conventional and spacer-type pearlescent pigments.

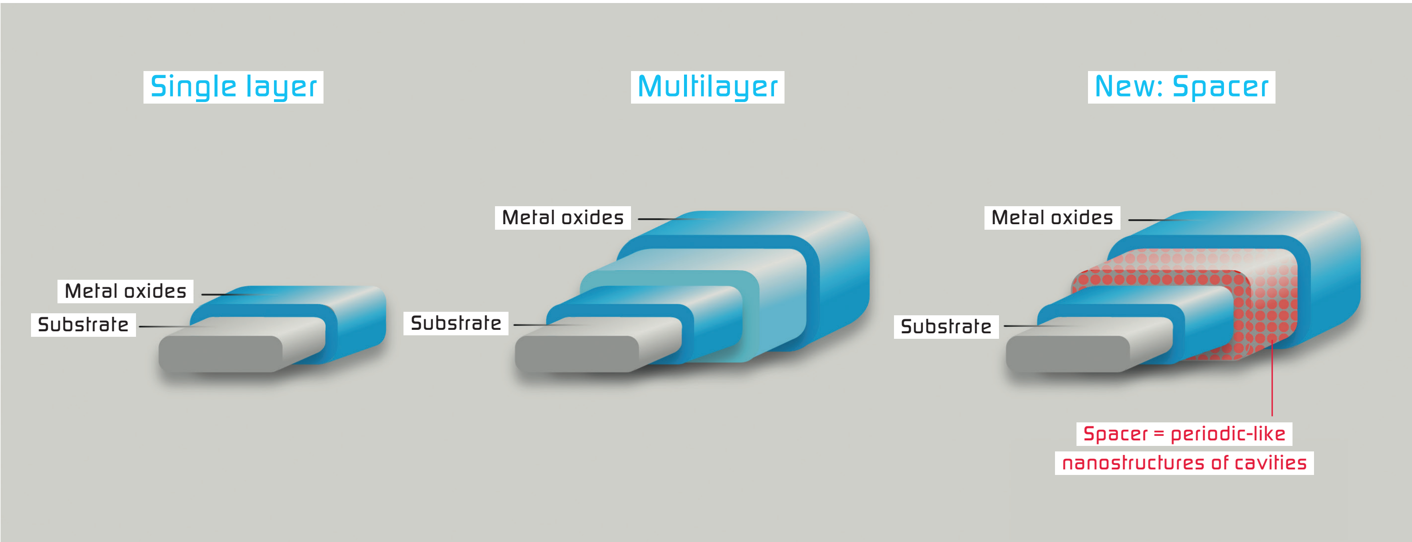


Figure 2: SEM cross-sectional images of spacer-type pearlescent pigments.

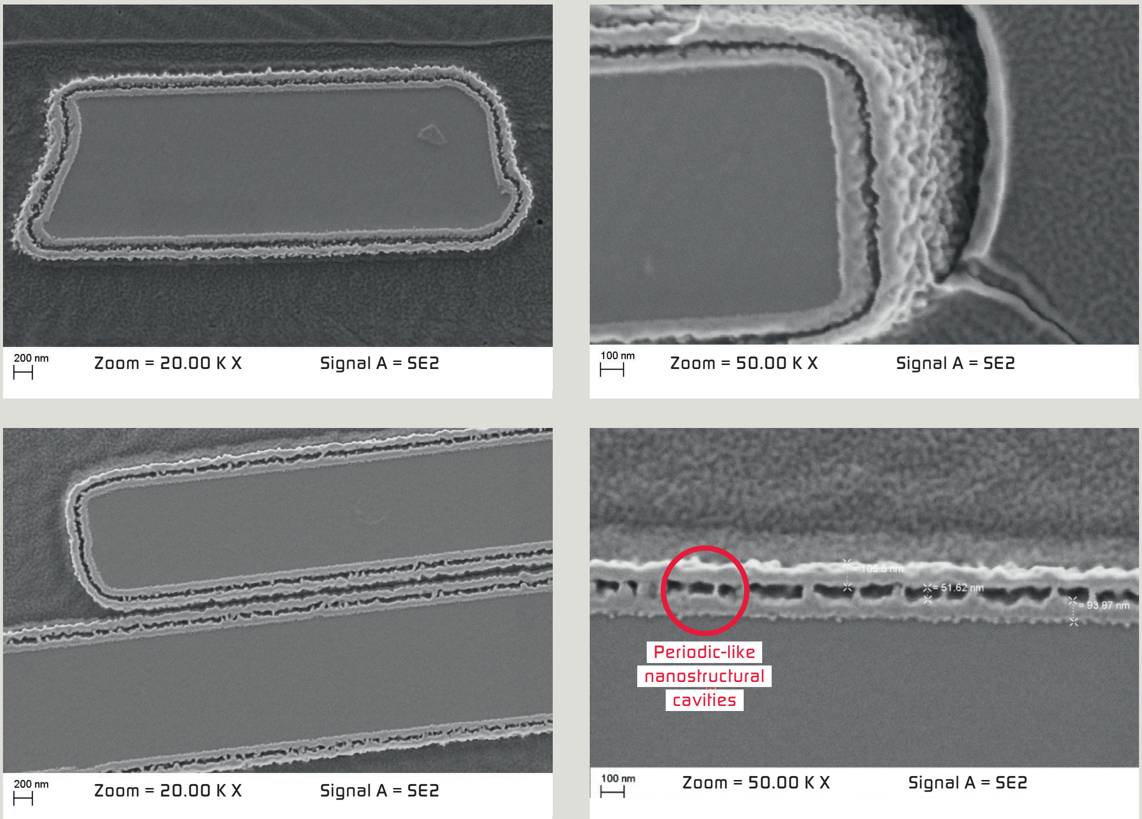
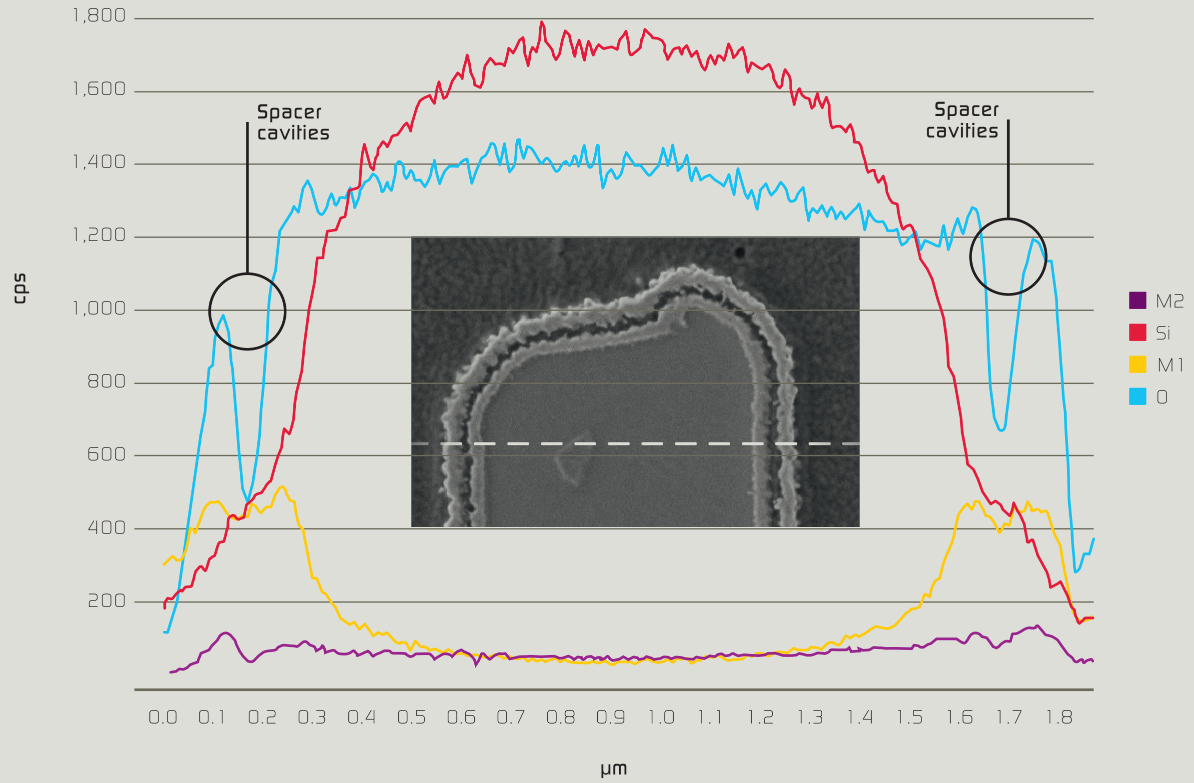


Figure 3: EDX analysis plot across spacer-type pearlescent pigment.



OUTSTANDING OPTICAL PROPERTIES

In general, as is well-known from conventional pearlescent pigments, all the colours of the rainbow can be realised with spacer-type products, too. All regulatorily approved materials can be used with this technology to generate corresponding spacer-type products.
On one hand, these include all typical platelet-like substrates, such as natural and synthetic mica flakes, glass flakes, silica flakes, and alumina flakes. On the other, all metal oxides of high refractive index, i.e. > 1.8, are also suitable, and they can be either transparent or semi-transparent and partly opaque. Typically, the oxides of Ti, Fe, Sn, Mn, Zr and Zn are the most suitable.
Careful selection and combination of metal-oxide types and metal-oxide thicknesses are key to generating the spacer element and are therefore what define the optical properties, i. e. reflection and absorption colour. Accordingly, special product designs offering superior or novel optical property combinations can be derived from this patented effect pigment class technology.

HIGH CHROMA

Most remarkable in terms of colour impression is the additional feature of the absorption colour of this pigment class, which can be designed to enhance the corresponding reflection colour even further. Consequently, the technology is ideally suited to creating a new level of high-chroma pearlescent pigments.
Examples of the optical properties of this effect pigment class are shown in *Figures 5* and *6*.
Compared with conventional pearlescent pigments ("Δ" in *Figure 5*), the significantly expanded colour space occupied by the spacer products ("O" in *Figure 5*) is striking. The straight colour lines of the spacer products are extended in the direction of higher colour intensity and have maximum colour values that are 30 to 60 % higher than those of conventional pigments. This linear-like colour behaviour confirms the visual impression. With change in viewing angle towards the gloss angle (15°), the colour strength increases, but without a noticeable change occurring in the colour shade or the colour angle. Unlike conventional interference pigments, spacer products combine intense interference colours with the corresponding absorption colour, which is also accompanied by high opacity. For example, synthetic mica-based spacer gold combines the golden reflection colour with a golden-yellow absorption colour to give a full golden impression when observed along almost the complete range of angles from 15 to 110°.
Figure 6 shows the chroma and sparkle values for synthetic mica-based spacer-type products in gold, orange, and red, as measured at 15° with a "BYKmac". The spacer-type products offer unique optical properties, and could therefore pave the way to original benchmark designs in the industry.

ANTI-FADING EFFECT AND SUPERIOR FLOP BEHAVIOUR

These optical properties and high-chroma features are now available in both the "Edelstein" and the "Luxan" series of pearlescent pigments.
The latest addition to the former series is a high-chroma "sapphire blue". This is designed to offer blue interference reflection and a unique dark-blue opaque absorption colour with unrivalled light-dark flop.
A special feature of such a combination, besides its optical performance, is the anti-fading effect demonstrated in *Figures 7* and *8*, which clearly show what is meant here by anti-fading.
While conventional interference blue effect pigments usually show significant fading and a pale look at higher observation angles, the high-chroma pigment exhibits a striking blue effect when observed over almost the full complement of angles, a fact which facilitates ultra-deep dark blue formulations with superior light-dark flop behaviour (*Figure 7*).

Figure 4: Theoretical background – simplified reflectivity model and equations.

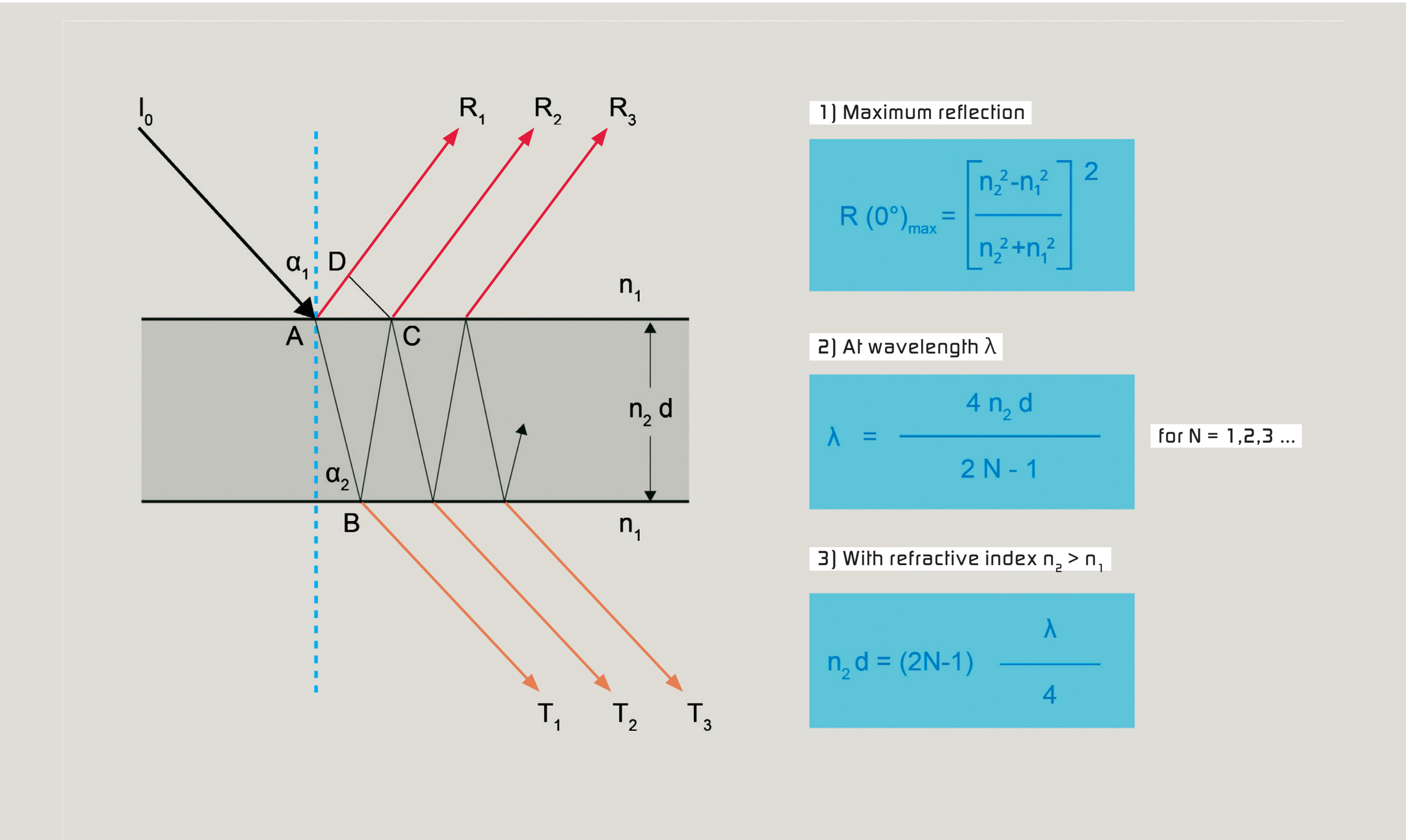
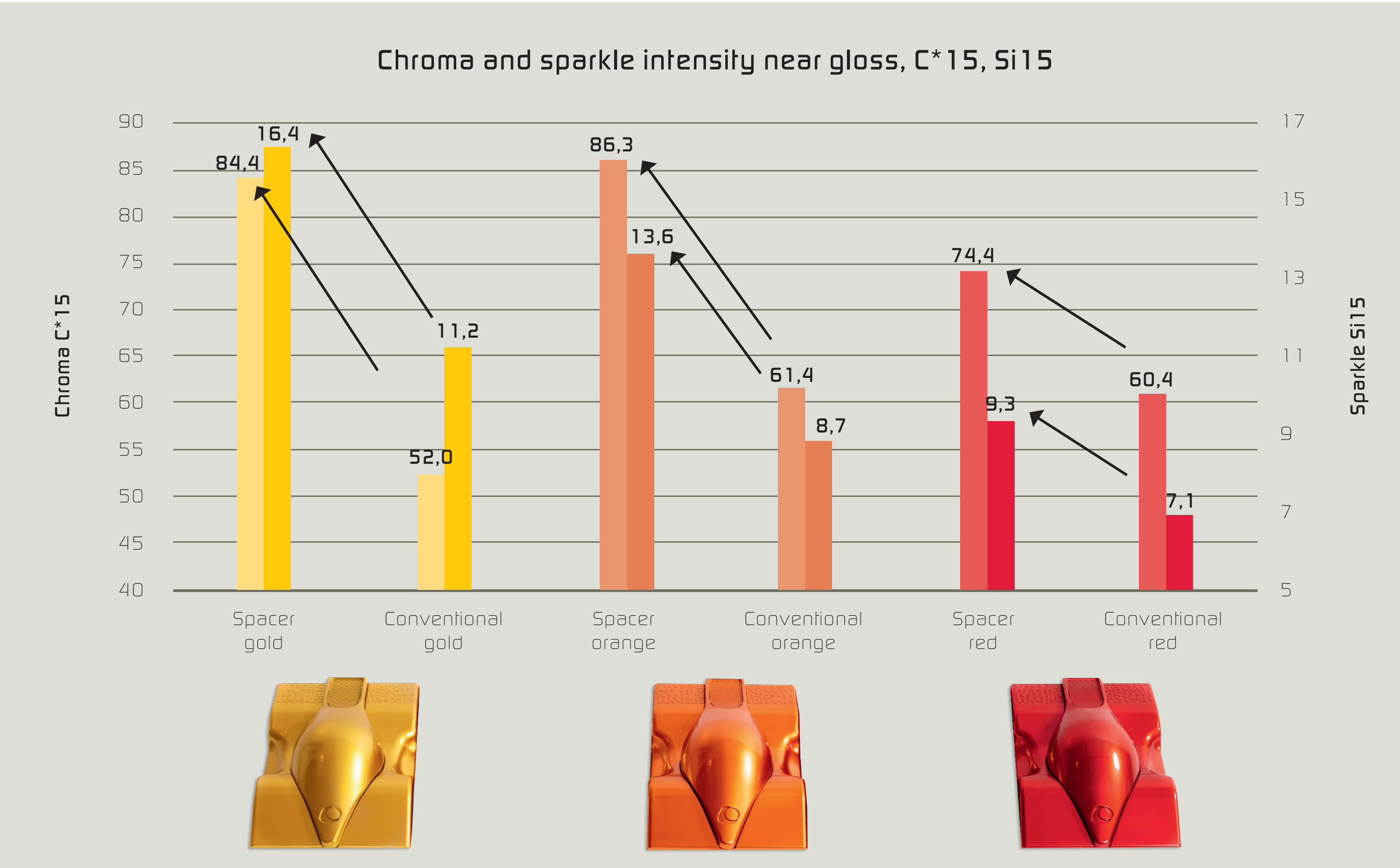


Figure 5: Angle-dependent colour measurement a* (red-green coordinate) and b* (yellow-blue coordinate).

Figure 6: Colour and effect measurement via BYK mac, colour intensity C*15 and sparkle intensity Si15.



Compared with other blue type interference pearlescent pigments, the high-chroma pigment shows a unique flop effect, with a flop value of 20.8 (versus 12.3 or 13.1 for others) and only quite low lightness of 8.1 at 110° (versus 26.4 or 20.6), while still providing intense blue chroma at 15° (*Figure 8*).

The best impression, however, is achieved by comparing coating applications on curved racing car panels. Regardless of observation angle and incident light source, the high-chroma pigment produces an intense blue and the highest lustre impression.

BETTER STABILITY

Besides optical performance, the spacer-type effect-pigment class is also notable for its stability, which in many cases is better than that of former high-performers in the industry.

Whether because of its chemical stability to aggressive media, bases or acids, and water, solvents or powder-based systems, or its superior UV durability in outdoor applications, such as OEMs or powder coatings, or its improved mechanical and shear stability, e.g. Waring-blender approved, this class of spacer-type pearlescent effect pigment offers universal applicability in basically all the relevant application systems and formulations.

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Figure 7: Angle-measurement model for anti-fading effect and panels.

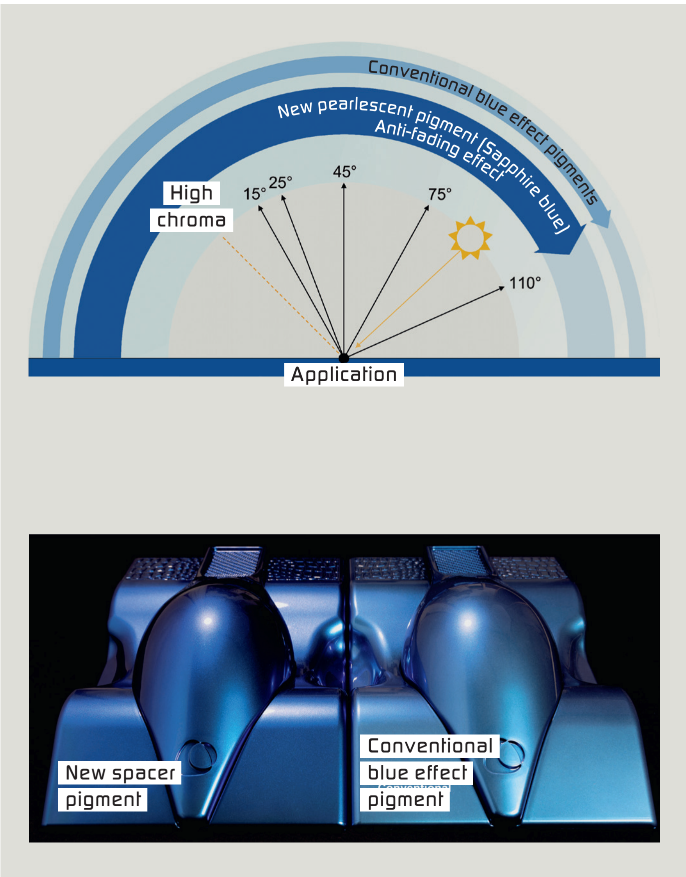

Figure 8: Measurement of lightness L*110°, flop and chroma C*15 of Sapphire Blue.