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GILDED SURFACES

Innovative mixing system with effect pigments.
By Dr Frank J. Maile and Dr Adalbert Huber, Schlenk Metallic Pigments, and Dr Jiri Filip, SightTex.

Source: Schlenk Metallic Pigments - mixing of ZENEXO(R) effect pigments in waterborne coating system

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Effect pigments based on ultra-thin pigment (UTP) technology can be used to create gold shades with exceptional hiding power and colour gamut for coating, printing and plastic applications [1]. Inspired by the ternary plot known from the metal alloys Au-Ag-Cu [2], three UTP-based effect pigments (YY-YS-OO) have been mixed using the innovative Zenexo ternary system (ZTS) to imitate gold shades. This paper looks at the new system and the device used to characterise appearance of samples prepared using the ZTS approach. Laboratory processes can be simplified and significant costs saved by combining both innovations.

Various effect pigments like pearlescents and metal pigments made of gold or copper-zinc alloys have long been used to decorate surfaces in a wide variety of applications. Colours in metallic elements and their alloys can be explained using band theory whereas (interference) colours in pearlescent pigments are formed by thin layers of higher refractive index deposited on semi-transparent substrates with platelet-like morphology [3]. With regards to the physics of Au-Ag-Cu alloys and their object surfaces, particle properties such as scattering at pigment edges and particle orientation must be taken into account when processing effect pigments in coatings, printing and plastics applications as they significantly influence the final appearance [4].

All pigments used in the ZTS are based on UTP technology and the pigment design shown in *Figure 1* centre. The core of the pigments is an ultra-thin, monolithic aluminium substrate with a typical particle size of 21 µm (D50) and a thickness less than 30 nm, resulting in an unprecedented aspect ratio (ratio of largest to smallest dimension), which is a prerequisite for a good flop. This aluminium substrate is coated with a low refractive index metal oxide and then iron oxide to obtain the desired interference colour. While silica and iron oxide layers can be deposited in precise thicknesses during pigment synthesis, conventional aluminium substrates cannot be produced in a very narrow thickness distribution. With UTP technology, the thickness of the aluminium substrates is negligible in relation to the overall thickness of the pigment, so that variations in the thickness of the substrate do not play a role - the pigments therefore all have the same thickness [1].

BENEFITS OF USING ZTS

The idea of using ZTS to exploit the extraordinary optical properties of effect pigments

RESULTS AT A GLANCE

→ Innovative Zenexo ternary system (ZTS) allows convenient imitation of gold colour shades in multiple applications (water/solvent-borne coatings, powder coatings, screen printing, plastics).

→ ZTS cornerstone pigments (YS-YY-OO) replace Au-Ag-Cu, exhibiting incomparable chroma, lightness and flop and creating a broad colour gamut.

→ Resulting colour shades create highly attractive and elegant surfaces due to unique properties of UTP technology-based effect pigments.

→ New measuring device allows convenient measurements due to flatbed scanner style providing broad spectrum of analytical tools in one device (incl. for effect coatings).

→ Data characteristics are captured in a single scan (reducing risk of manipulation with samples) and high-resolution interactive visualisation of effect coatings on any shape is provided.

based on UTP and generate a mixing system was inspired by the well-known Au-Ag-Cu ternary system [2], which is the basis of the most commonly used gold jewellery and dental alloys today. By varying the composition of the Au-Ag-Cu system, a variety of hues and colours can be obtained, as shown in the ternary phase diagram in *Figure 2*, right. It can be seen that adding Cu gives the alloy a reddish hue, while adding Ag turns the alloy greenish. This is consistent with band theory as silver causes an increase in the energy gap that electrons must overcome to reach an energy state above the Fermi level [5].
Using the Au-Ag-Cu ternary plot, three pigments were synthesised using UTP technology. The optical properties of the three corner pigments (YY-YS-OO) based on UTP and used in the ZTS are discussed in detail in [1], the most important pigment benefits are reviewed here. The thickness of the aluminium substrate was reduced to a minimum and the weight percentage of aluminium in the pigment is less than 15 %. The pigment can be handled as a dry powder and, as confirmed by the German Federal Institute for Materials Testing, is neither flammable nor explosive. Such pigments can be marketed as a powder without need for solvents or hazardous goods labels. In addition to safety benefits, the 100 % powder product allows more accurate dosing and easier formulation of water-borne or sensitive coatings with high solid content.

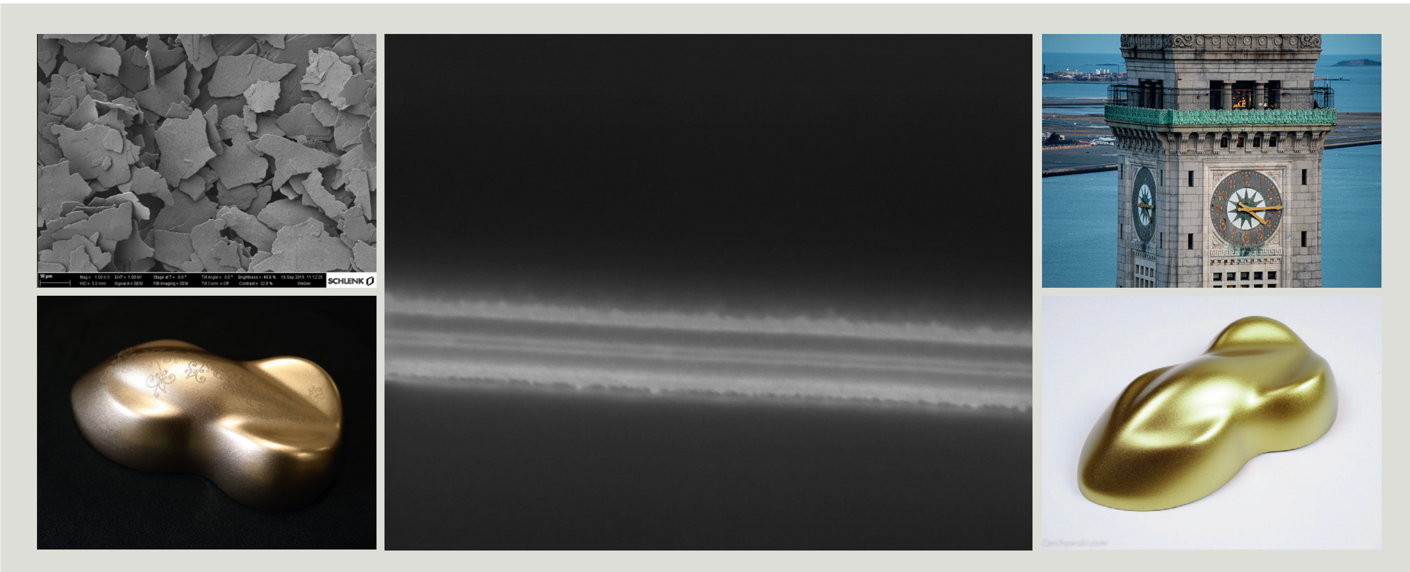
EASY MIXING AND PROCESSING

The colorimetric and physical properties of effect pigments based on UTP represent perfect starting conditions for a mixing concept. This is because the pigments can be processed in various applications like powder coatings, water/solvent-borne coatings, printing inks and in plastics applications, where they can develop their coloristic properties. The UTP types YY-YS-OO can be easily mixed due to similar physical particles properties and do not display segregation (e.g. in dry-blend applications resulting in highly chromatic powder coatings) in the final application. Intrinsic laser marking properties (see *Figure 1*) result in not haptically perceptible markings. These advantages can be transferred to all applications as shown in *Figure 3* and *Figure 4*.
As dispensing is simple, the desired golden shades in the ZTS can be accurately pigmented or worked out.

WIDE RANGE OF APPLICATIONS

Figure 3 shows the new ternary system (YY-YS-OO) based on UTP pigments, where the metals Au-Ag-Cu were replaced at the corners by the respective effect pigments. Here, the ZTS system is based on an aqueous automotive basecoat, sprayed pneumatically using a HVLP gun and a spraying robot onto small ABS speed shapes for better visualisation of colour and flop. In order to define the samples used and their designation, we will refer to ZTS Coatings (ZTS CO), as well as powder coating (ZTS PC), (screen) printing (ZTS PR) and ZTS P (plastic injection moulding) applications, *Figure 4*.
The ZTS approach works excellently in individual applications, however, the colour shades in the positions in the respective ZTS ➜

Figure 1: Effect pigments based on UTP technology in micro/macroscopy: SEM images (cross-section, top view). Speed shapes sprayed with gold/white-gold colour shades using a water-borne automotive basecoat. Laser mark can be seen on white-gold part. UTP pigment (YY) on the watch hands of the Boston clock tower as a substitute for gold leaf.



for one application cannot be compared with the other on a colorimetric level. Even if the percentage composition is identical applications in one position in the ZTS, other factors contribute to the realised shade differing in colour and on a colorimetric level. The respective ZTS should therefore be considered as a starting point and formulation aid for the elaboration of golden shades similar to Leuser's (Au-Ag-Cu) ternary system, in which the desired target shade can be decided and then – within an application – realised by mixing the respective, pure starting components (YY-YS-OO). The final pigmentation level is then also taken into account, depending on the respective application and the customer's system. Further fine-tuning of the final composition to achieve the desired gold shade can be done by the customer himself, leading to know-how protection on the formulation side.

A NEW MEASURING DEVICE

In order to better understand and characterise the ZTS of the individual applications, a novel device was used, which allows both appearance characterisation and the visual measured data display.
The Sighttex Q [7] is a device for sensing the appearance of materials [8]. It consists of 5 high-resolution industrial RGB cameras mounted in-plane at angles of 15°, 30°, 45°,

Figure 2: Visualisation of the relationship between colour and composition (for Ag-Cu) in the ternary Au-Ag-Cu shown on the right [2]. Adding copper in increments (by 10%/w) gives the alloy a reddish hue [6].

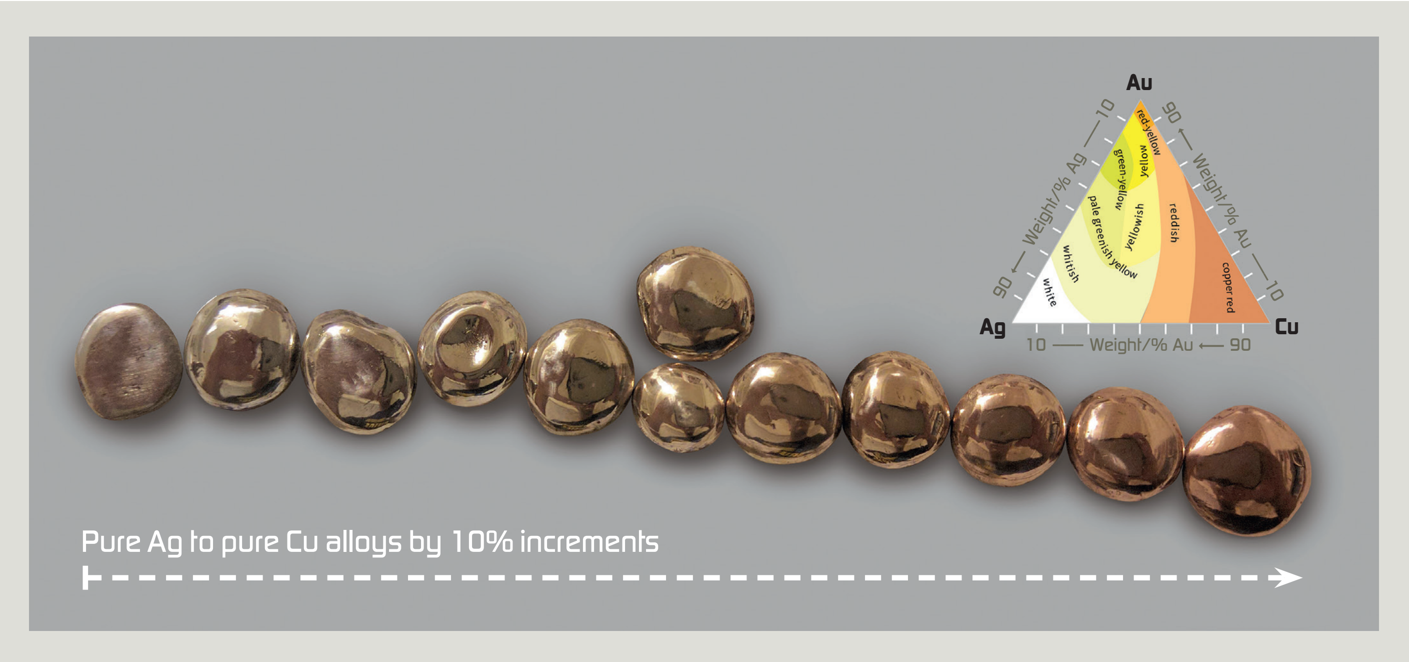
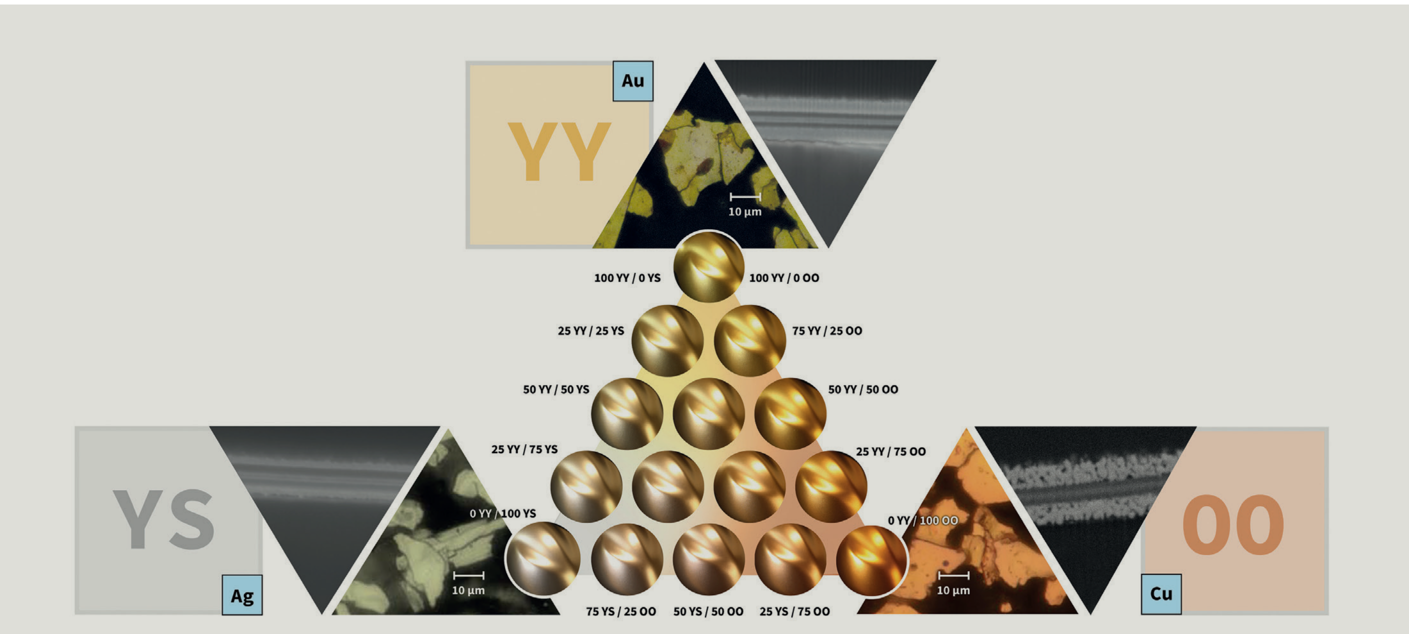


Figure 3: The new ternary system based on UTP pigments for water-borne coatings (ZTS CO): the metals Au-Ag-Cu were replaced at the corners by the respective effect pigments (YY-YS-OO). Electron (cross-cut through individual pigment structure) and light microscopy (top view, BF, 1000x) of the three cornerstone UTP pigments.



60° and 75°, and 28 LED point lights mounted in-plane at 3° increments between 0° and 81°. Cameras and lights allow independent adjustment of any azimuthal (out-of-plane) angle from 0-360° with 0.1° repeatability. The instrument can capture the appearance of the material with a resolution of up to 1500 DPI, which corresponds to a pixel-size of 17 μm (59 pixels/mm). This configuration provides a wide variation of geometries that can be captured, giving the device versatile capabilities. The device is used as a standard flatbed scanner with the material sample positioned over a 40 mm aperture at the top of the device, as shown in *Figure 5*. Because of this design, nearly flat parts of non-flat objects can also be analysed.

NUMEROUS TOOLS AVAILABLE

The device can capture visualisation data in several material-specific modes, which enables interactive viewing and illumination of a user-defined geometry. It also captures detailed statistical and texture data for quality control and other applications. Accompanying software offers colour, reflectance and texture analysis. Coating-specific tools allow analysis of gloss, sparkle and graininess, comparison of textures and statistics for in-plane geometries. A particle distribution tool estimates particle inclination and anisotropy distributions. The photometric tool provides an estimate of the normal, albedo and elevation maps of the material per pixel. The versatility of the instrument allows data for the above analyses to be collected in a single scan that takes between 2 and 40 minutes, minimising the need for sample manipulation on different analysis platforms.

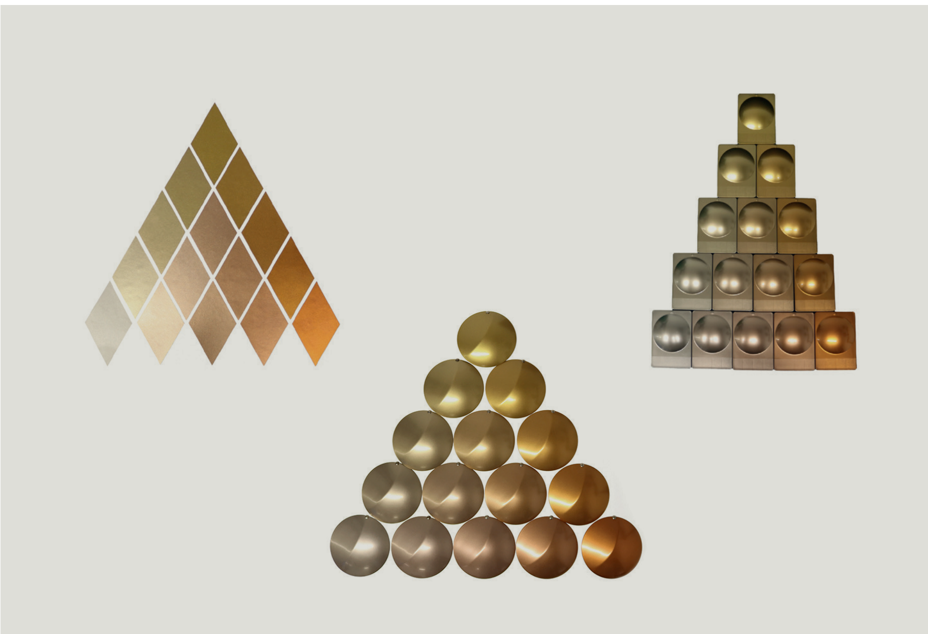
A COMPARISON OF THE ZTS APPLIED TO DIFFERENT APPLICATIONS

All samples of 15 ZTS colour shades were captured for four different applications (PC, PR, CO, P), then collected and visualised on a blob shape as shown in *Figure 6*. As the data collected include the behaviour of the coatings under different illumination and viewing geometries, it is possible to display a "virtual layer" on literally any 3D object shape. Colour analysis of the acquired samples in the CIELAB colourspace revealed significant differences in luminance and chromatic behaviour between the tested application methods, as shown in *Fig. 7* for the 45°/30° (45°/as15°) near-specular geometry. When comparing the luminance values, we observe higher values for ZTS PR and ZTS CO. The same behaviour can be observed with respect to the colour scale, with ZTS PR and ZTS CO showing significantly higher values, especially in the b* channel.

COLORISTIC EVALUATION OF A SELECTED COLOUR SHADE

However, regardless of the known differences in the applications studied, it was necessary to characterise and compare the individual ZTS samples (PC, CO, P, PR) from *Figure 3* and *Figure 4*. As an example, one colour shade containing all three UTP pigments was selected, containing 50 % OO, 25 % each of YY and YS. This colour shade was then produced in different applications as shown in *Figure 3* and *Figure 4*.

Figure 4: The new ternary system (YY-YS-OO) based on UTP pigments in other applications: printing (ZTS PR, left), powder coating (ZTS PC, middle), and plastics (ZTS P, right).



A side-by-side comparison of the virtual object covered with this specific shade with the raw captured texture is shown in *Figure 8*, left. With 28 lamps, the device can provide 55 sampling points for a dense in-plane comparison of the selected colour shade in a range between [-81°, 81°] (step in polar angle 3°). A comparison of the ZTS applications in the CIELAB colourspace is possible using luminance and a-b diagrams. The luminance plot revealed that ZTS PC and ZTS PR have higher near-specular intensity and much narrower specular peak compared to ZTS PR. Similarly, we can observe differences in the colour gradient in the a-b diagram, where the colour gradient of ZTS P is clearly different from that of the other compared methods. It is possible to assess texture images for any captured geometry as for standard ASTM geometries.

FLOP, GLOSS, SPARKLE AND GRAININESS

The flop index (Alman) readings for the individual application methods were compared with gold leaf. Results for the selected colour shade are shown in *Figure 8* (right, a). The highest values comparable to gold leaf were obtained for ZTS PR and ZTS CO.

The gloss analysis provides readings of standard gloss geometries at 20°, 60°, 85°, contrast gloss, DOI, haze index and haze at 2° from specular – some of these results are given in *Figure 8* (right, b). The highest gloss values are obtained for ZTS P, while the lowest are obtained for ZTS PR. For the sake of validation, a correlation study for Sighttex Q readings comparing other devices obtained high Pearson correlation values 0.956/0.932 at geometries 20°/60°.

The sparkle analysis of the selected colour shade for illumination geometry 30° (as -15°) in *Figure 8* (right, c) shows that a higher sparkle area S_A was identified for ZTS PC and ZTS P, while the sparkle intensity S_I is the highest for ZTS PC. Similarly, for the sparkle grade S_G, the different applications can be ranked in the following order: ZTS PC > ZTS PR > ZTS CO > ZTS P. Obtained correlations to the industrial device for $S_A/S_I/S_G$ were 0.912/0.896/0.869. The estimated graininess G for the selected colour shade has similar ranking, i.e., from the highest values to the lowest: ZTS PC > ZTS PR > ZTS CO > ZTS P. A correlation to the industrial device was 0.883.

PARTICLE ORIENTATION

While the analysis of colour, gloss, sparkle and graininess has become the industry standard, the instrument also allows the characterisation

Figure 5: Sighttex Q device. Left: demonstration of flatbed acquisition of sprayed coating samples for visualisation and analysis purposes. Right: available in-plane geometries (bold arrows represent viewing geometries).

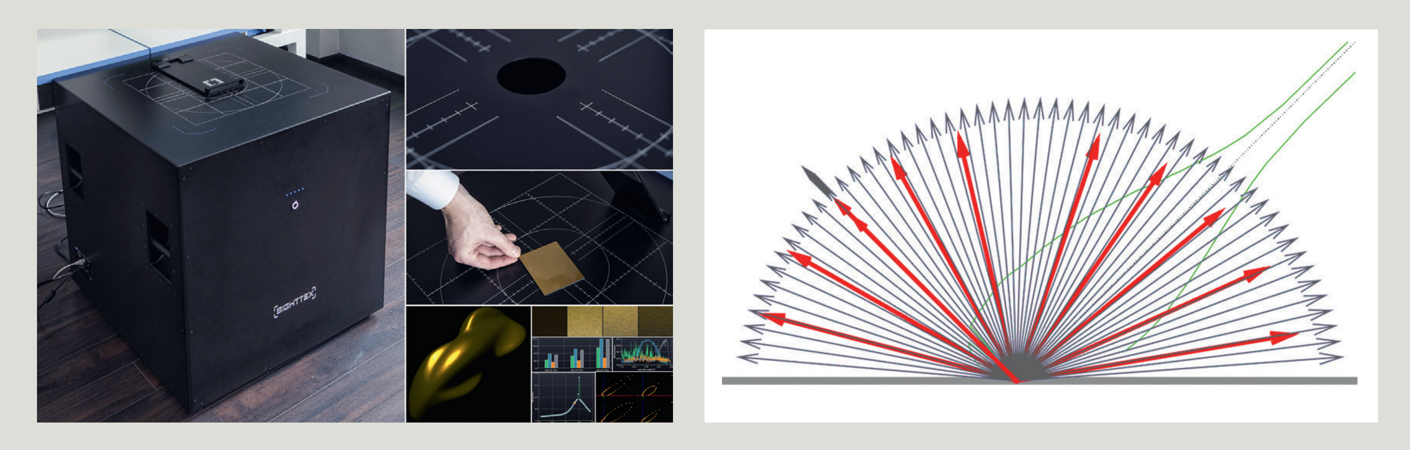


Figure 6: Visualisation of all captured ZTS colour shades for the different applications in Fig. 3 and Fig. 4.

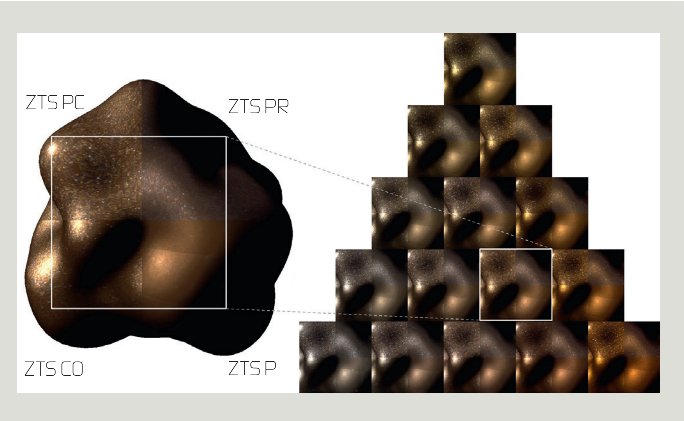


Figure 7: Colour analysis for all applications shown in Fig. 3 and Fig. 4. in CIELAB colourspace for the near-specular geometry 45°/30° (45°/as15°). The selected colour shade is denoted by a square marker; pure UTP cornerstone pigments (YY-YS-00) are denoted as triangles.

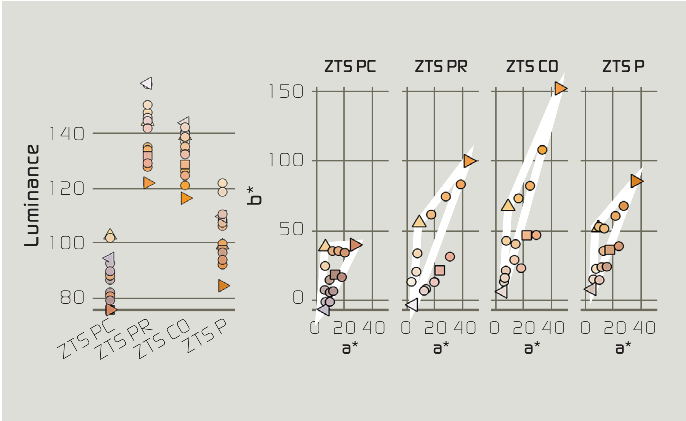
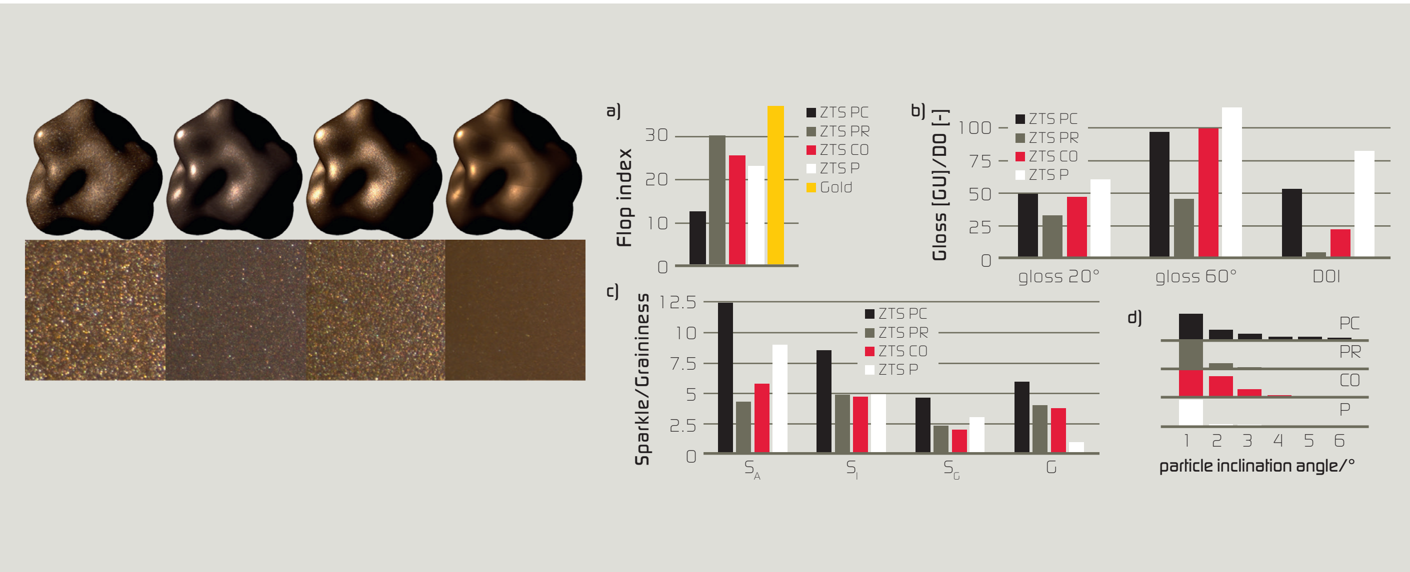


Figure 8: Selected ZTS colour shade in all applications (from Fig. 3 and Fig. 4). Left: visualisation on a 3D object, captured texture on area 8 x 8 mm (500x500 pixels at 1500 DPI) for standard geometry 45°/0° Right: readings for the selected colour shade: (a) flop index (Alman) compared to gold leaf, (b) gloss and DOI, (c) sparkle/graininess, (d) histograms of particle inclination angles.



of particle orientation, presented as histograms of the (1) inclination and (2) azimuth angle of the platelets to the surface normal. The former is suitable for the analysis of typical flake alignment along the surface, while the latter is suitable for the analysis of anisotropic effects in the material structure. Since the ZTS samples do not exhibit any anisotropy in principle, only the histogram of the inclinations of the effect pigment particles is shown in *Figure 8* (right, d).

SUMMARY

In conclusion, it can be said that the combination of both innovations creates customer benefits because, on the one hand, the new ternary system (ZTS) based on the three basic pigments (YY-YS-OO) enables the rapid formulation of gold colour shades in a wide range of applications, and, on the other hand, the new measuring device enables rapid and comprehensive characterisation of the surfaces produced, simplifying laboratory processes and saving costs.

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