Reflections on the right angle

Interference colour measuring systems must show physical plausibility

Contact:
Werner Rudolf Cramer
T +49 251 58188
wrcramer@muenster.de

Werner Rudolf Cramer

The use of colour measuring systems designed for use with solid colour pigments or reflective metallics to assess interference-type pigments may cause problems. Modern effect pigments may create very large colour shifts as the viewing and illumination angles. Thus the choice of measurement angles is critical. Some white calibration standards may be unsuitable for use with interference pigments.

The use of interference pigments in the automobile and other industries since the mid-1980s has led to a growing concern with their visual and instrumental colour matching. In many cases, the methods used for coloured and aluminium pigments have simply been applied – and are still being applied – to interference pigments without considering their differing optical characteristics.

These methods are subject to as little scrutiny as are the functions of the measuring instruments themselves that are intended to record the optical characteristics of interference pigments. These characteristics are different from other types of pigment. Coloured pigments absorb some of the light that falls on them and reflect the rest of it in a non-directional way. Aluminium pigments reflect the incoming light at a consistent angle and, depending on their type, may create very bright effects. Interference pigments can show much more complex optical behaviour.

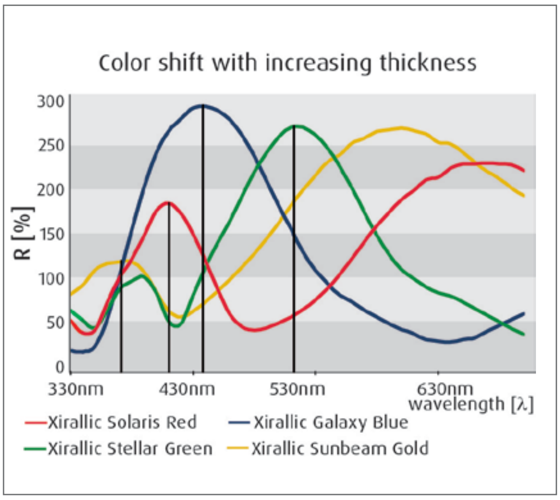

Figure 1: The reflection maxima shift towards longer wavelengths. Two different reflection maxima are involved here, so that layer thickness is actually greater on the blue and green pigments than on the yellow and red

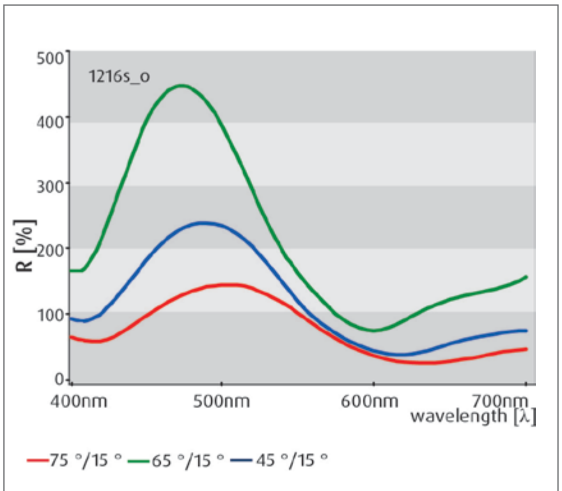

Figure 2: Reflectance curves shift towards shorter wavelengths, while differences between the maxima increase ("Xirallic Turquoise T60-25" (1206s_o) is shown, illuminated at 15 °, 45 ° and 65 ° and measured at 15 ° from the gloss angle)

Design and optical properties of interference pigments

Interference pigments mainly consist of a transparent carrier material coated with a metal oxide with a high refractive index, such as titanium dioxide or iron oxide. This composition creates selective reflection: part of the incoming light is reflected directly when it strikes the surface. The rest of it makes its way through the layer of metal oxide and is refracted, before some of it is then reflected at the boundary layer between the metal oxide and the carrier. This reflection leaves the metal oxide in parallel to the first reflection, which creates interference between the two parts.

The rays of light that penetrate the pigment also create interference and produce the transmission colour. Because of the absence of a phase shift – which occurs only at a transition from an optically less dense to an optically denser medium – this is complementary to the reflection colour. The reflection colour depends in particular on the type of metal oxide coating, the thickness of the layer and the angle of the incoming light.

When measuring the colour of interference pigments, the physical values of the reflection are recorded. They say more about the optical properties than the L*a*b* values calculated from them. And these reflectance values and curves make it possible to identify physical plausibilities that allow conclusions to be drawn about the characteristics and behaviour of the interference pigments.

Layer thickness controls colour of effect pigments

Even if the simplified interference law only provides approximate information about reflections and refractions, it does reveal the important factors on which the resulting colour depends: the thickness of the layer of metal oxide is directly proportional to the wavelength of maximum reflection. As the layer is made thicker, the

maximum reflection therefore shifts towards a longer wavelength.
If the carrier layer is coated with only a little titanium dioxide, it reflects the whole spectral range and creates a white effect. If the layer is thicker, the reflection plateau shifts further towards a long wavelength and at the same time a minimum shifts from the invisible UV range into the blue-violet range. This creates a yellow colour.
As the thickness of the coating increases, the colour changes to red. Thereafter a maximum moves from the UV range into the blue range, following the minimum previously mentioned, while at the same time the first reflection plateau shifts further into the invisible IR range. And if the layer becomes thicker still, the maximum shifts to green (*Figure 1*).

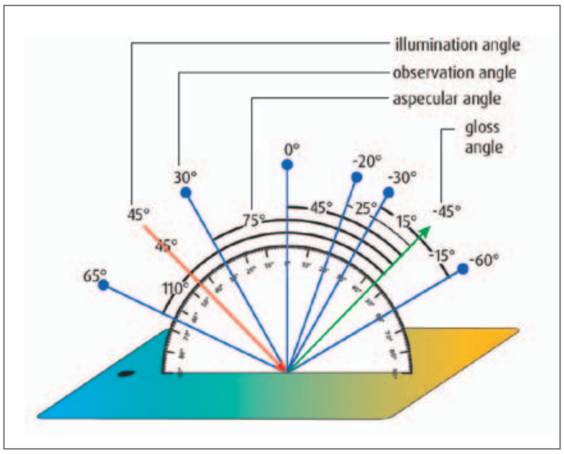

Figure 3: Definition of the measurement geometry as set out in ASTM E2539 Standard Practice: measurements are taken from the gloss angle which results from an illumination angle of 45 °

Effects of angle of illumination

The different layer thicknesses are created during production of the pigments; the user can only use the colour and therefore the layer thickness requested without any changes. However, the user does have the opportunity to change the angle of the incoming light for visual and instrumental colour assessment of interference pigments: the interference formula shows the inverse proportionality of the illumination angle to the reflection maximum. With a flatter illumination angle, the maximum shifts towards the short wavelength spectral range. The appearance of a green interference pigment changes from yellow-green with a steeper illumination to blue-green with flatter illumination. A red interference pigment changes its maximum towards yellow (as yellow has a shorter wavelength than red) with flatter illumination and towards blue with a steeper illumination, as a maximum from the UV range shifts further into the visible range.
While interference pigments of the “Iriodin” type only display small, but visible, shifts (approx. 30 nm), these are significantly larger with “Xirallic” pigments which use aluminium oxide flakes as the carrier material. Even stronger and clearer colour changes can be found with “Colorstream” pigments with SiO_2 carriers. Here colour shifts from green through yellow to red-violet can be observed, as with “Viola Fantasy”.

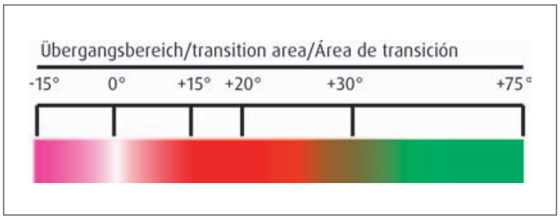

Figure 4: Outside the transition area (between 20 ° and 30 ° from the gloss angle) absorbent characteristics predominate

Results at a glance

››› The nature and design of interference pigments is briefly described and the effects of changing the angle of illumination and viewing are considered. Modern types may be designed to create very large colour shifts as viewing and illumination angles change.

››› Physical plausibility of different interference colour measuring systems has been checked.

››› At angles close to the gloss angle, the transmission colour of an interference pigment may be combined with its reflection colour. Thus for comparison purposes it is important to use an instrument with a measuring angle 15 ° from the gloss angle.

››› Some white materials used as calibration standards behave inconsistently at flatter illumination angles, and opal glass should be considered the most suitable standard to use when interference pigments are being studied.

Figure 5: If transparent interference pigments are applied over a white background, the change from reflection to transmission colour is clear in the transition area between 20 ° and 30 ° from the gloss angle

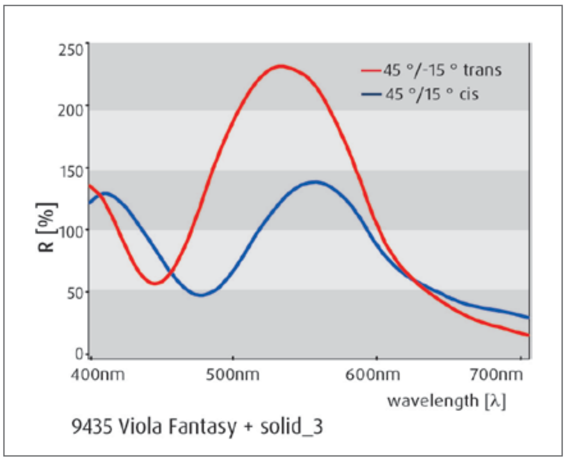

Figure 6: "Colorstream Viola Fantasy" mixed with coloured pigments shows the shift of the reflectance curves towards shorter wavelengths and the increase in the maximum when changing between "cis" and "trans" measurements

A further factor must be added to the interference formula, which can be derived from the Fresnel equations: the flatter the angle of illumination on the interference pigments, the greater the increase in the reflection maximum. And the differences between the maxima become greater, the flatter and larger the angle of incidence (*Figure 2*).
In summary, two factors and properties can be identified that typify the optical characteristics of interference pigments:

» With an increasing angle of incidence and therefore with flatter illumination, the reflection maximum shifts towards shorter wavelengths.
» At the same time, the differences between the maxima increase.

When assessing the plausibility of measurement results in particular, these two factors play a fundamental role. If they are not reflected in the results, it can be assumed that the measurements are faulty. In this respect, it is worth checking the reflectance values of measurements of interference pigments or paints that contain them. Firstly, the physical plausibility of the measurements can be checked. And secondly, it is possible to make more precise statements about the interference pigments with regard to identification and characterisation.
In practice, it is only laboratory equipment that offers the possibility of measuring from various illumination angles, for example from 15 ° to 65 ° from normal. As a result of structural and technical requirements, portable devices normally only offer one or two illumination angles, which are also set out in the ASTM standard E2539.

Selecting suitable measurement geometries

Colour measurements are not normally carried out at the gloss angle, but at defined differential angles (aspecular). As a result of the introduction of portable devices with a limited geometric range and the establishment of specific differential angles, measurements are traditionally made at 15 °, 25 °, 45 °, 75 ° and 110 ° from the gloss angle. These geometries are also defined in the ASTM Standard Practice E2539 on the measurement of interference pigments (*Figure 3*).[1]
Depending on the requirements of the user, the colour measurement devices may either have all of the geometries that were originally suggested for the measurement of metallic paints and aluminium pigments, or just a selection of them. These have then been applied without modification to the measurement of interference pigments.

[1] The differential angle is usually given, not the viewing angle, and the viewing angles are given a minus sign, which is not physically correct.

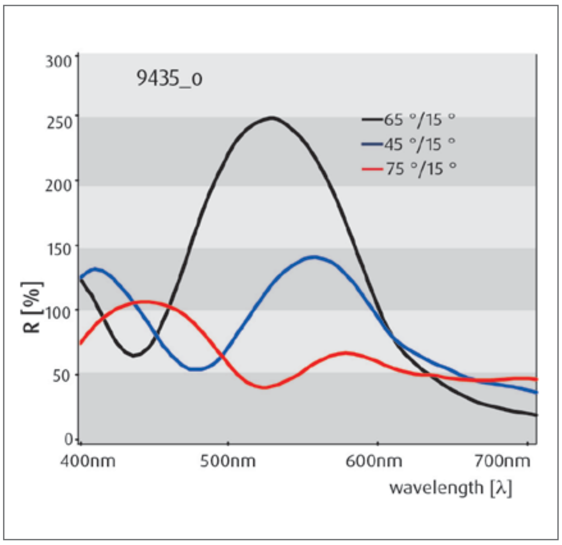

Figure 7: Plausible results of a measurement of sample 9435 ("Colorstream Viola Fantasy" + colour blend solid_3): the measurement curves shift towards shorter wavelengths and the maxima become greater when the illumination is at a flatter angle

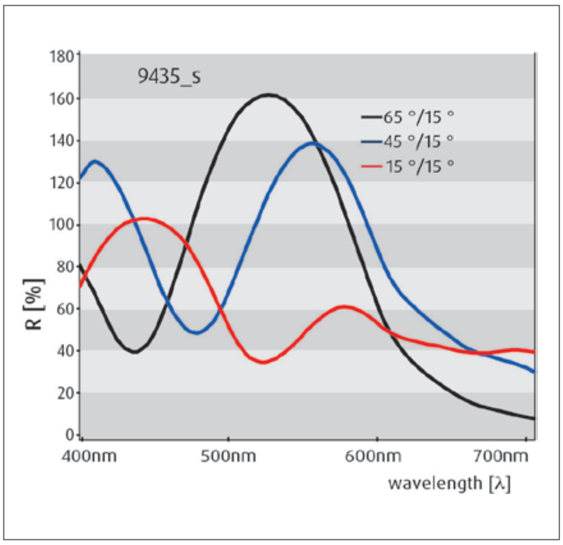

Figure 8: The same sample 9435 as in Figure 7 measured after calibration with "Spectralon": the curve shifts towards the shorter wavelengths when the illumination is flatter, but the maximum does not increase accordingly


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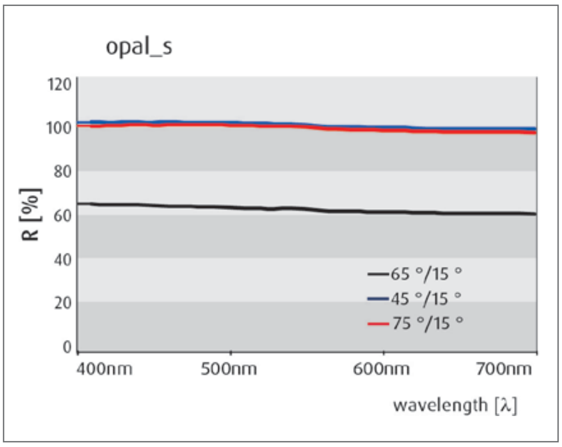

Figure 9: Measurement of the calibration materials (calibration with "Spectralon" and measurement of opal glass) shows their differences with flat illumination: the reflectance curve for flat illumination would also be app. 100 %

In the measurement of transparent interference pigments, the relationship between the reflection colour and the complementary transmission colour becomes clear: if transparent interference pigments are applied to a white background, the complementary transmission colour is reflected by it. Close to the gloss angle, it is then added to the reflection colour and weakens it in comparison to the same pigment on a black background.

If one moves further away from the gloss angle and therefore the differential angle increases, one can observe and measure a transitional range between 20 ° and 30 ° of difference to the gloss angle. Above 30 °, only the transmission colour can be observed and measured (*Figure 4*). From this it can be concluded that:

» The reflection colour, also known as the interference colour, can only be measured at 15 ° from the gloss angle (*Figure 5*);

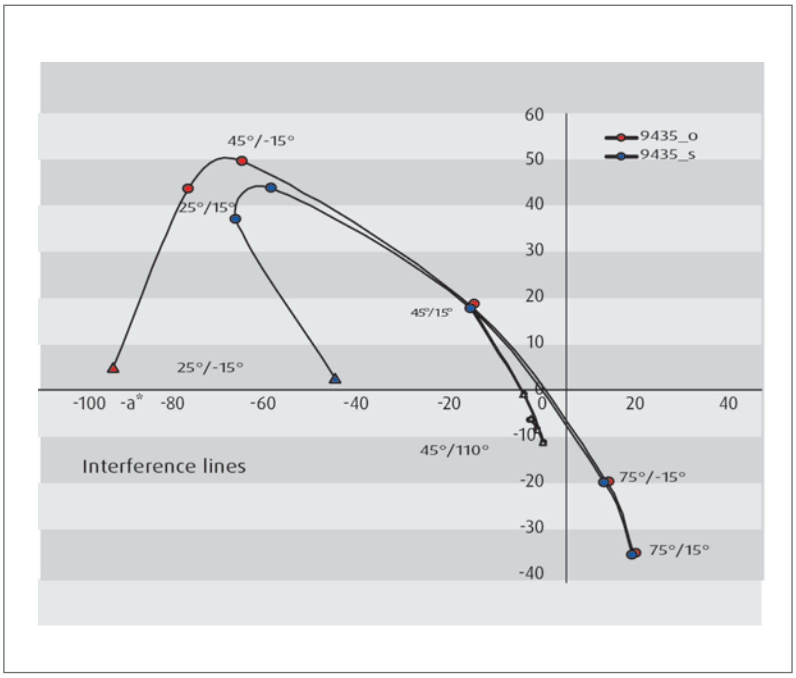

*Figure 10: The L*a*b* presentation of the measurement results provides no indication of their plausibility*

» A transitional area exists between 20 ° and 30 °, which depends on the type of interference pigment;

» Scattering and undirected reflective components predominate at angles more than 30 ° from the gloss angle.

From these aspects, it can also be concluded that measuring instruments without a 15 ° differential angle cannot measure interference colours. Smaller differential angles, such as 10 ° from the gloss angle, only provide plausible results for samples without clear lacquer.

Cis and trans geometries yield different results

Measurements can be made on both sides of the gloss angle: "cis" geometries are those in which the illumination and measurement angle are on the same side as the gloss angle; "trans" geometry is the term used if they are on the opposite side to the gloss angle. Modern measuring instruments use both classical geometries and a trans geometry of -15 °. This geometry is also described in the ASTM Standard Practice E2539.

A rough estimate of the measurement results for this trans geometry suggests that the values correspond approximately to those of cis geometries that are illuminated at an angle of 15 ° flatter. It must be emphasised that this is only an approximate estimate and it merely serves as a guide. The measurement results are certainly not the same!

Nevertheless, the measurement results for coloured interference pigments reveal two aspects here (*Figure 6*):

» Changing from cis to trans geometry, the reflectance curves shift towards shorter wavelengths with the same angle of illumination.

» Likewise, the maxima increase in trans geometries compared to those in cis geometries.

Both aspects can also be used to address the question of the plausibility of the measurement results. (With aluminium and white interference pigments, there is no colour shift: the reflectance curves shift almost in parallel).

Calibration requires a whiter shade of pale

The question of the calibration material is surely as old as colour measurement itself. Barium sulfate, opal glass, ceramic and more recently PTFE (polytetrafluoroethylene) such as "Spectralon" or "Fluorilon" are some of the different materials used for calibration of white.

The material that should be used in combination with interference pigments is also evident from the results of the measurements: if these are plausible in terms of optical physics, the results can be accepted. The plausibilities are also used to check the calibration and the instruments themselves (*Figure 7*).

Usually, samples and specimens are illuminated at 45 ° or 15 ° from normal. With these illumination geometries, there are usually no problems in relation to plausibility. But when the illumination is flatter, deviations may become apparent that rule out a calibration material, showing it to be unsuitable for measurements of interference pigments. If one calibrates a device from various illumination angles and the same differential angles, according to the plausibility rules outlined above, the maxima of the reflectance curves should shift towards the shorter wavelengths and rise increasingly. Calibrations with PTFE do not show these plausibilities for flat illumination (*Figure 8*).

In order to draw further conclusions, the calibration materials can also be measured against one another. To do so, the first material is used as the calibration material and the second material is measured. If, for example, calibration is carried out with "Spectralon", the reflectance curve of bright opal glass for an illumination of 65 ° from the gloss angle and a differential angle of 15 ° is significantly below 100 (*Figure 9*).

Measurements of interference pigments therefore show no physical plausibility if the device is calibrated with "Spectralon" and the measurements are carried out with flat illumination geometries. The typical interference behaviour can only be identified in measurements following calibration with bright opal glass (*Figure 10*).[2]

To summarise, interference pigments constitute an important group of pigments in the automobile and other industries. Their properties in terms of optical physics are indicated primarily by their physical reflectance values. Only as a secondary step $L^*a^*b^*$ values should be used for assessment, since only reflectance values can be used to identify and check physical plausibilities.

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[2] The same sample of "Viola Fantasy" was measured after calibration with "Spectralon" (9435_s) and after calibration with opal glass (9435_o).