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RAINBOWS MADE TO ORDER

The effective use of interference and polychromatic colorants. By Werner Rudolf Cramer, free consultant, and Frank J. Maile, Carl Schlenk.

Interference pigments can deliver a wider range of optical effects than other pigment types, since their angle-dependent behaviour involves superimposing light waves rather than purely absorbing or reflecting them. Factors affecting the appearance of these pigments are discussed and the use of diffraction pigments is considered.

Interference pigments are among the most optically sophisticated pigments. Unlike colour pigments that absorb some of the incident light and metallic pigments that reflect it, interference pigments involve superimposed light waves that are shifted together due to reflections and refractions. This causes strengthening or weakening of the resulting light waves. Various factors, such as the structure of the pigment, its application and the lighting, make for optimum conditions.

Pigments manufactured with wet chemistry generally have a carrier platelet of natural mica, silicon dioxide or aluminium oxide. High refractive index metal oxides such as titanium dioxide or iron oxide are applied to this carrier platelet. Depending on the layer thicknesses of the oxide, these pigments change their colour from white, yellow, red or blue to green. This unusual colour shift results from the fact that the maxima - and also the minima - move to longer wavelengths. For yellow, the minimum shifts from the UV range into the visible region, while white becomes a yellow. If the layer thickness of titanium dioxide is further increased, this minimum shifts further into the longer wavelengths, which results in a red. The maximum following the minimum in the UV range migrates into the visible range, while the maximum in the long wavelength range travels into the invisible infrared range.

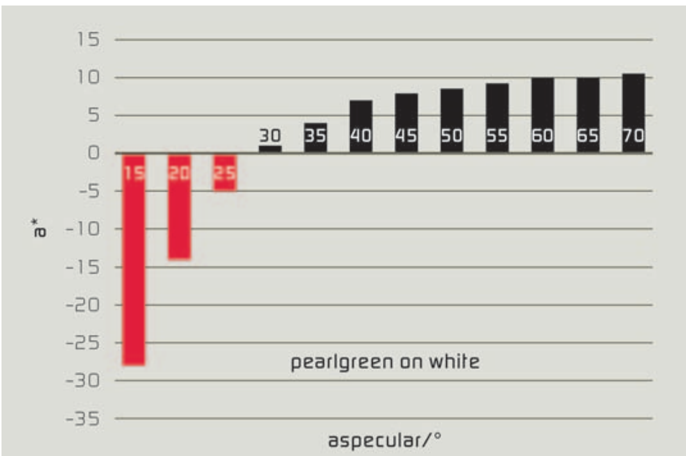
With higher layer thickness the blue maximum shifts into the green range. Such pigment group colour sequences are thus chemically identical, differing only in the layer thickness.

ORIENTATION, ANGULAR AND SUBSTRATE EFFECTS

Interference pigments have been used in automotive paints since the mid-Eighties. Since that time, there has been increasing interest in quantifying their colours and effects. They are applied as so-called basecoats, which are then sealed with a clear coat. These basecoats have a layer thickness of 10-15 µm; the interference pigments are in the range of 5-100 µm long and about 0.05 µm thick. Due to their size, the pigments can only be situated as platelets lying more or less parallel to the coating layer in the paint. This orientation is enhanced by additives during the drying process of the basecoat. The theoretical calculation of the orientation of the pigments on the basis of measuring angles must therefore be studied.

Patterns in the electron microscope show a relatively flat orientation; in the light microscope, the change in the illumination angle shows that the colours observed almost always arise from the type of pigment and not from differently oriented pigments. Most interference pigments are transparent, which is why the colour of the background or environment also plays a role. Since the incident light is divided into the reflection colour and complementary transmission colour, the change can be observed well on a white background.

Figure 1: Up to 25° aspecular, both the reflection and transmission colours are observed when the transparent pigment is applied over a white background. The transmission colour is absorbed over a black background.



RESULTS AT A GLANCE

→ Interference pigments can deliver a wider range of optical effects than other pigment types, since their angle-dependent behaviour involves superimposing light waves rather than purely absorbing or reflecting them. Their appearance depends largely on the thickness of the high refractive index material applied to the carrier platelet.

→ Factors affecting the appearance of these pigments are discussed, as well as the differing effects that can be obtained by mixing them with other types of pigment or changing the underlying paint colour.

→ The use of diffraction (polychromatic or 'rainbow effect') pigments is also discussed. These pigments used alone always show a complete rainbow as the viewing angle is changed, but adding colour pigments can suppress part of it.

→ The use of mixtures of different types of pigment and different background colours allows a vast range of effects to be achieved.

With measurements close to the gloss angle, the reflection colour is detected and the transmission colour is removed from the gloss. This transmission colour is produced on the opposite side of the pigment, reflected by the white background. If angular differences are measured aspecular with an illumination angle of 45°, the reflection colour in the range can be detected up to about 20°. Between 20° and 30° aspecular there is a so-called transition range.

With large aspecular angles, the complementary transmission colour that is reflected from the white background is measured. A black background absorbs the transmission colour. Coloured substrates as well as admixtures of colour pigments show similar patterns (see *Figure 1*).

MEASURING THE APPEARANCE OF INTERFERENCE PIGMENTS

The laws of optics describe three properties that can be applied to interference pigments. On the one hand, the reflection maximum shifts to shorter wavelengths when the illumination is flatter. This is a crucial property for the characterisation and identification of interference pigments. This optical property can be technically measured in that the illumination angle is changed from a steep angle to a flatter one or vice versa, while the aspecular angle remains constant for each gloss angle. This results in a typical interference line for the individual pigment. An aspecular angle of 15° has proved particularly useful here. Measurements at aspecular angles closer to the gloss often run the risk of giving implausible measurements, especially when it comes to samples with a clear coat. The second property is demonstrated in the changes of the reflection curves. They not only shift to a shorter wavelength, but their maxima rise considerably with flatter illumination. As a result of this property, the interference line in the a*b* colour space diagram always runs in a counter-clockwise direction with flatter illumination. Thus, the colour of a red interference pigment shifts from bluish red to yellowish red, and a green shifts from yellowish green to bluish green. The third characteristic relates to measurements at constant illumination: commonly, a constant illumination angle of 45° is recorded, but other angles such as 65° are possible. Since all interference pigments show their reflection colour – which can also be measured – close to the gloss angle it can also be observed and measured even in unusual mixtures with colour pigments.

Thus, the blue reflection colour is retained even if the corresponding pigment is mixed with a green or red colour pigment. Basically, an effect arises from the fact that the colour and/or brightness changes depending on the geometry. And with interference pigments the reflection colour is always detected close to the gloss.

HOW ADDING OTHER PIGMENT TYPES AFFECTS APPEARANCE

The overall colour appearance of a pigment mixture is affected differently by the pigments it contains. This applies to the colour pigments, aluminium pigments and interference pigments. Colour pigments affect the overall colour impression across all geometries, aluminium pigments close to the gloss and interference pigments mainly up to about 25° aspecular. Thus, the colour of the interference pigment is affected by the colour pigments, as they also reflect close to the gloss. But measurements at a constant illumination angle and varied angular differences to each gloss angle are not limited to an illumination angle of 45°. In principle, 45° illumination has simply emerged as the most suitable for characterisation.

The combination of these measurements results in the so-called 'aspecular line'; the combination of the measured values at a constant differential angle is referred to as the 'interference line'. Again, the indication of the aspecular angle is necessary because there may be multiple connection lines. At an aspecular angle equal to or greater than 30°, the transmission colours are measured with transparent interference pigments on a white background.

ALL THE COLOURS OF THE RAINBOW IN ONE PIGMENT

In addition to the known interference pigments, which are prepared by wet chemistry or in a high vacuum, there are special types of interference pigments. Their optical response corresponds to reflections on a diffraction grid. The incident light is spectrally fragmented, from blue-violet over blue, green, yellow to red.

Unlike 'normal' interference pigments, which show a colour gradient depending on the angle of illumination, a complete rainbow is always evident in the polychromatic pigments. Their colours can be measured individually - the eye has a greater observation and detection range than a measuring instrument and sees a complete rainbow.

The range of the rainbow lies in an angular range of 20 to 30 degrees depending on the angle of illumination. With flat 65° illumination the rainbow starts at about 45° and extends to about 75° aspecular. With

steeper illumination at 45°, the range shifts from 35° to 65°. These are the limits for the colours of the first order. The colours of the second order follow in this range; they are measurable, but barely visible.
From the reflectance curves it is clear that the reflections and their maxima shift from the UV range into the visible range as the aspecular angle increases in relation to the gloss angle. With further increases in the aspecular angle they leave the visible spectral range, moving into the infrared region, while maxima of the 2nd order move from the UV into the visible range (see *Figures 2* and *3*).
The interference laws - the shift of the reflections to shorter wavelengths with flatter illumination - also apply to these pigments. Presuming aspecular geometry – for example, at 55° – and if the reflections of different illumination angles have this constant differential angle, the shift of the maxima to shorter wavelengths with flatter angles of illumination can be clearly seen. Thus, in these pigments, the optical reflection laws apply both on the diffraction grid and in terms of interference.

MODIFYING THE APPEARANCE OF EFFECT PIGMENTS

Interference pigments have typical reflection colours with a small or large colour gradient. They are found in many car colours in combination with colour and aluminium pigments. In order to create a blue colour effect, for example, a white interference pigment can be mixed with a blue colour pigment. Instead of the white interference pigment a blue or green may also be used. The possibilities for combinations here are almost infinite.
In the case of polychromatic pigments, the combinations are made rather differently: admixtures of colour and aluminium pigments influence the polychromatic rainbow effect. Polychromatic pigments are inherently silver-white to silver-grey from their base colour. The rainbow effect occurs most clearly with these neutral pigments. Admixtures of colour pigments suppress the rainbow partially or even completely, so that in principle some preliminary considerations are necessary.

- The complete rainbow exists only in polychromatic pigments alone or with minimal admixtures. To retain the rainbow, the possibilities for combination are limited. Admixtures of black are ideal, because in this case the rainbow colours are not affected. And because of the greater contrast, the rainbow effect is more intense. When such pigments are used, the full rainbow is always seen; there are no pigments which show only a half or a quarter of the rainbow. In this case the effect must be controlled with admixtures with other pigments (*Figure 4*).

Figure 2: At 25° aspecular, no maximum is detectable in the visible region. When the aspecular angle is increased, the maximum shifts into the visible region and moves away from it again at or above 65° aspecular.

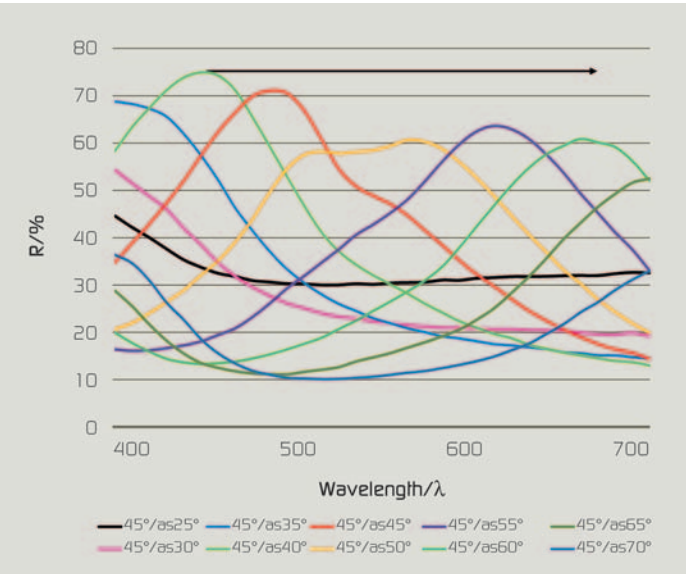


Figure 3: The colours of the rainbow flow clockwise in the a*b* diagram. Modern colour instruments detect the rainbow at 45° and 75° from gloss.

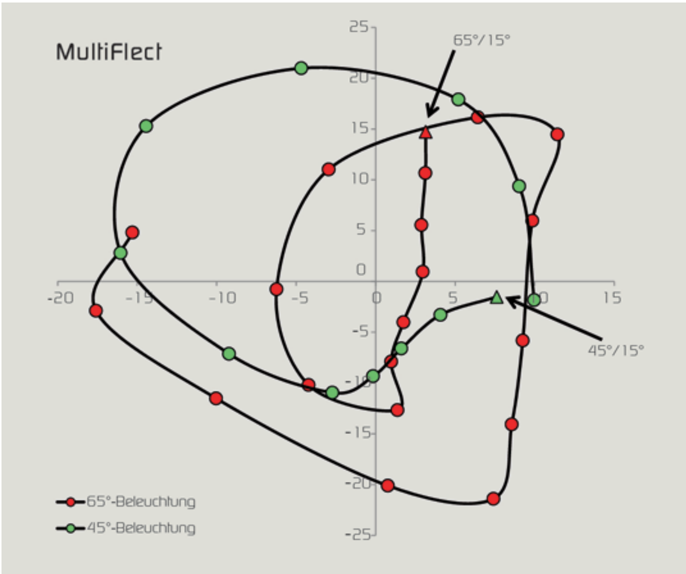


Figure 4: Different pigment concentrations reflect the rainbow in various strengths.

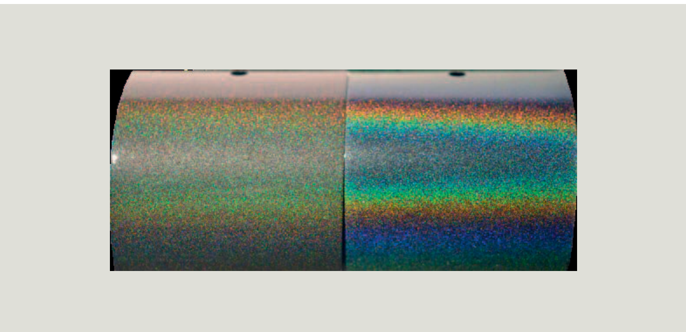
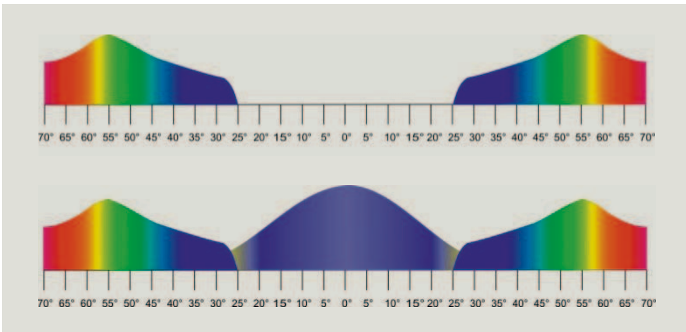


Figure 5: The rainbow can be observed on both sides of the gloss angle (top); an interference pigment that shows its reflection colour at up to 25° aspecular is placed in this 'gap' (bottom).



- The rainbow starts at about 35°-45° aspecular; interference pigments show – depending on the type – their reflection colour up to about 25° aspecular. In this respect, two colour ranges can be used by mixing both types of pigment.
- Looking at a spray-out of a polychromatic pigment from above, one can detect the 'gap' between the two rainbows on either side of the angle of observation. An interference pigment can be incorporated that so to speak fills this 'gap'. Such mixtures can be created in various ways, where the selected colour of the interference pigment may also affect the rainbow (see *Figures 5*, *6* and *7*).
- Admixtures of colour pigments influence the colour impression over the entire illumination and observation range. Depending on the shade of the colour pigment, the rainbow is affected and may no longer be recognisable in its entirety.
- Like the colours of the interference pigments, the rainbow appears intense only in a narrow angular range. Despite their relatively lower intensity close to the gloss, colour pigments produce a stronger overall colour impression. As such, they often have a strong influence on the rainbow, which can only demonstrate a strong presence in combination with dark colour pigments.

DETAILED EXAMPLE OF MIXING DIFFERENT PIGMENT TYPES

Examples of mixtures of a pigment of this rainbow type called "MultiFlect" with blue colour pigment and blue interference pigment show the respective influences in the geometrics areas: near the gloss at 15° aspecular - in this case with an illumination of 45° - the rainbow pigment reflects with a slight valley in the green range; away from the gloss angle - in this case at 50° aspecular - the green of the rainbow can be seen. By adding a blue pigment, the 45° aspectral reflectance curve shifts to higher values, above all in the blue spectral range; close to the gloss the 15° aspectral reflectance curve is slightly increased in the blue and red range. The differences in mixtures with blue interference pigment are even more distinct. Their reflections close to the gloss affect the resulting reflectance curve with a strong maximum at 15° aspecular. The reflections of this pigment shift, so to speak, between the rainbow reflections of the special effect pigment. This optical behaviour can also be observed visually: left and right of the gloss the rainbows can be seen as well as the blue interference colour between them. Interference pigments in other colours provide the same results, where their reflection colour provides a more or less strong contrast to the rainbow. Plotting the a*b* values shows a shift of the rainbow circle into the blue area with the addition of a blue colour pigment. The addition of a blue interference pigment causes the unfolding of this circle in the blue region. Experiments with different colour pigments and interference pigments show similar colour responses.

MAKING MOST EFFECTIVE USE OF POLYCHROMATIC PIGMENTS

As with all effect pigments, the use of polychromatic pigments requires an intensive examination of illumination and observation geometries, if useful and interesting colour creations are to be produced. Although these pigments 'only' show a rainbow, admixing interference pigments in particular can create effects that exploit the optical properties of both types of pigment.
In addition, colour pigments can be used, which can have a crucial effect on the overall colour across all geometries. Starting from the polychromatic pigment, different approaches for colour creations can be implemented.
Certainly the use of this type of pigment is particularly limited in the automotive sector, but it can be used for attractive concepts in special series. This requires detailed knowledge of the geometric constraints of the colours. The difficulty in developing this knowledge stems from the fact that the geometries of the rainbow are only partially recorded by the measuring geometries of most spectrophotometers.

LITERATURE

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Figure 6: The initial values of the rainbow are shifted toward the admixed interference pigment. As anticipated, the influence of the polychromatic pigment predominates at or above 35° aspecular.

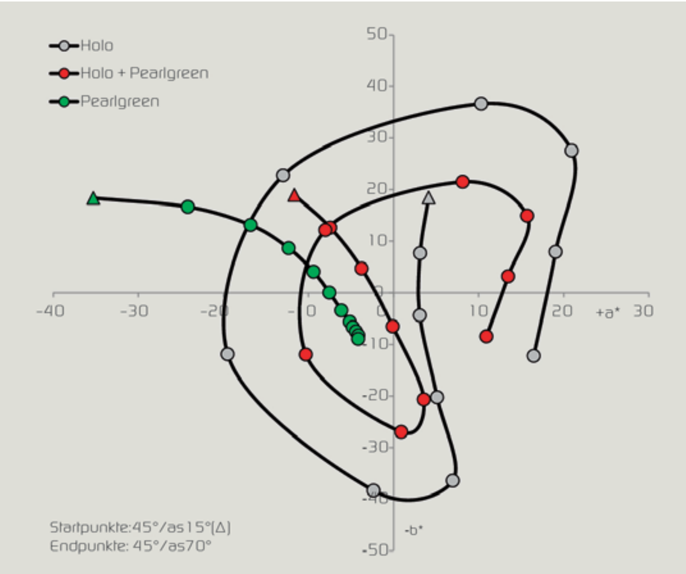
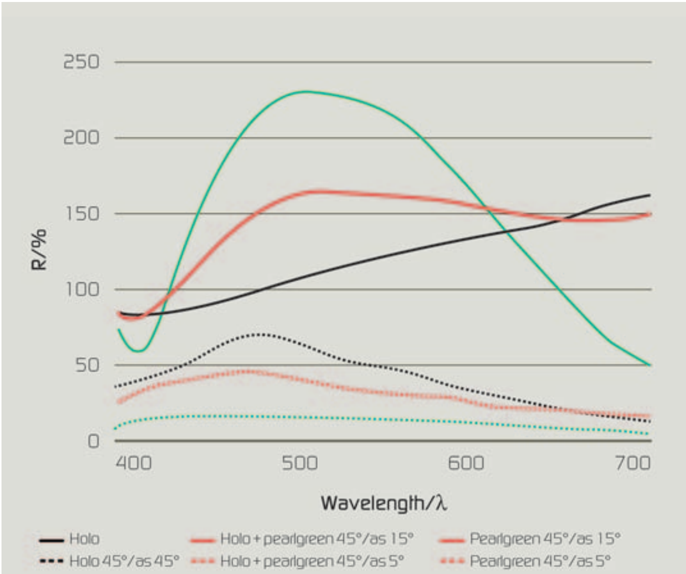


Figure 7: The reflectance curves also show the combination of the optical properties of both pigments: the mixture shows colour reflections both close to the gloss as well as away from it.



“Individuality is in the foreground.“

3 questions to Werner Rudolf Cramer

For which applications are polychromatic pigments most suitable? *With polychromatic pigments a variety of applications are possible – everywhere where special effects are desired. Automotive coatings, industrial and powder coatings are only some examples in which effects are in demand. With this kind of pigment – as with all effect pigments – individuality is in the foreground.*

Does it make sense to only use polychromatic pigments – as opposed to a combination with other types of pigments? *Through combination with other pigments, the range of possible applications is increased. In this respect, the decision will depend on the application: what should be in the foreground, the individual effect or the total colour impression of the combination with other pigments?*

Can the optical properties of mixing diverse pigment types easily be obtained? *There are two main points that help facilitate the introduction into the mixing behaviour of different kinds of pigments: firstly, it should be noted that two different mixing behaviours encounter each other, namely the subtractive and additive mixing. Secondly, it is always worth looking at the reflectance curves, which show the real optical behaviour of effect pigments.*

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