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APPLIED THEORY ARTICLE

Visual and instrumental assessment of interference pigments

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Abstract
Discrepancies often exist between visual assessment and instrumental assessment. These are due to different geometries with which samples are viewed or measured: In visual observation at the window or in the light booth, the sample panels are usually moved up and down. This changes the angle of illumination and observation. The current measuring devices have a fixed illumination.

KEYWORDS
anchor form, angle of illumination, angle of observation, color measurement, difference angles, instruments, interference pigments

1 | INTRODUCTION

For the characterization and identification of interference pigments, the use of color measuring instruments is a matter of course today. The automotive industry in particular places high demands on the color accuracy of the automotive coatings it supplies. This applies to both series and refinish coatings. Compared with coatings from other industries or even other applications such as plastics, automotive coatings consist of a combination of different pigments which, in addition to color, are also intended to absorb fluctuations during application.

For these reasons, instrumental assessment is just as important as visual assessment. And both should deliver the same results. Unfortunately, supposed discrepancies due to incorrect and insufficient knowledge appear again and again. In 2008, after lengthy deliberations, ASTM (Subcommittee E12.12) established the test methods for measuring interference pigments (Figure 1). Unfortunately, not all specifications were adopted by the manufacturers of measuring instruments. Until today, this has led to the fact that interference and interference pigments can only be measured inadequately by the portable measuring instruments (Figure 2). In addition, the samples are incorrectly handled during visual sampling.[1]

Interference pigments—except for the white interference pigments—change their color depending on the angle. It is therefore important in their evaluation to find which measurement geometries (illumination angle: observation angle) are used. The pigments consist of a carrier platelet coated with a strongly refractive metal oxide. In most cases, the carrier platelets consist of a transparent material (eg, natural or artificial mica) and the metal oxide of titanium dioxide, which is transparent in these layer thicknesses. When light falls on the surface, it is split there. One part is directly reflected with phase shift (thinner medium into denser medium). The other part penetrates the strongly refractive metal oxide layer with refraction. At the boundary layer to the carrier platelet, one part is again reflected, leaving the pigment parallel to the first part. The other part continues to travel through the pigment with refractions and reflections and leaves it on the underside. The resulting color is complementary to the reflection color on the upper side. This change between reflection and transmission color can be observed if the interference pigment is applied to a transparent foil or a white substrate. In the case of the foil, the reflection color is seen in the top view and the complementary transmission color in the see-through view. From a white background, the transmission color is observed away from the gloss, while close to the gloss the reflection color appears (Figure 3).

The two parts that leave the pigment at the top interfere with each other, resulting in the amplification

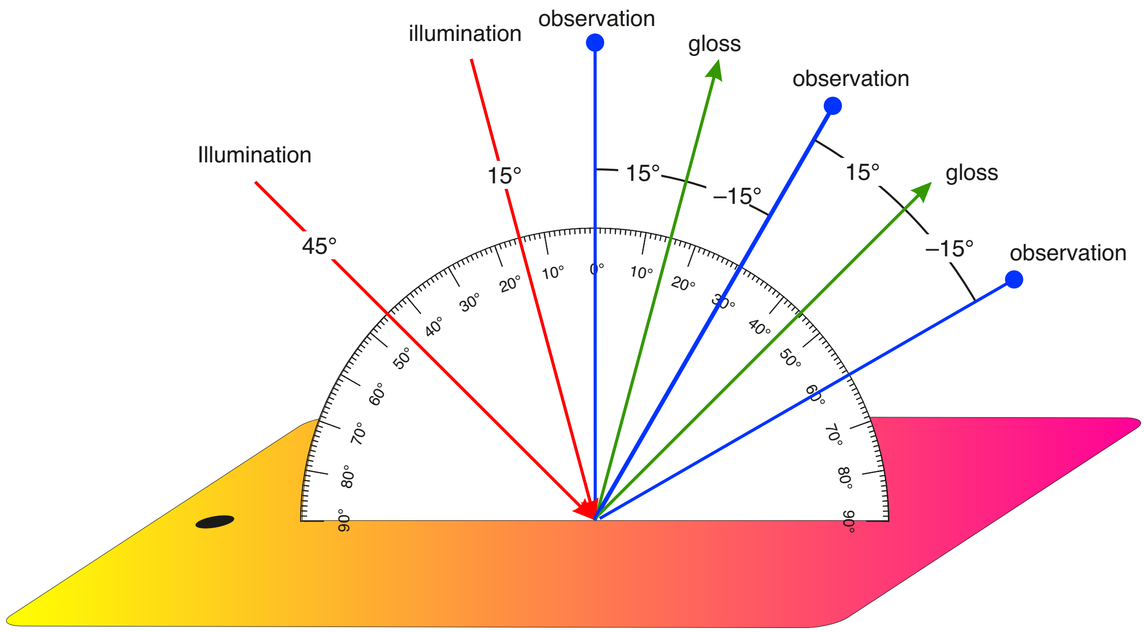

FIGURE 1 The ASTM test method E2539 describes the additional geometries for measuring interference pigments at two illuminations of +15° and −15° aspecular

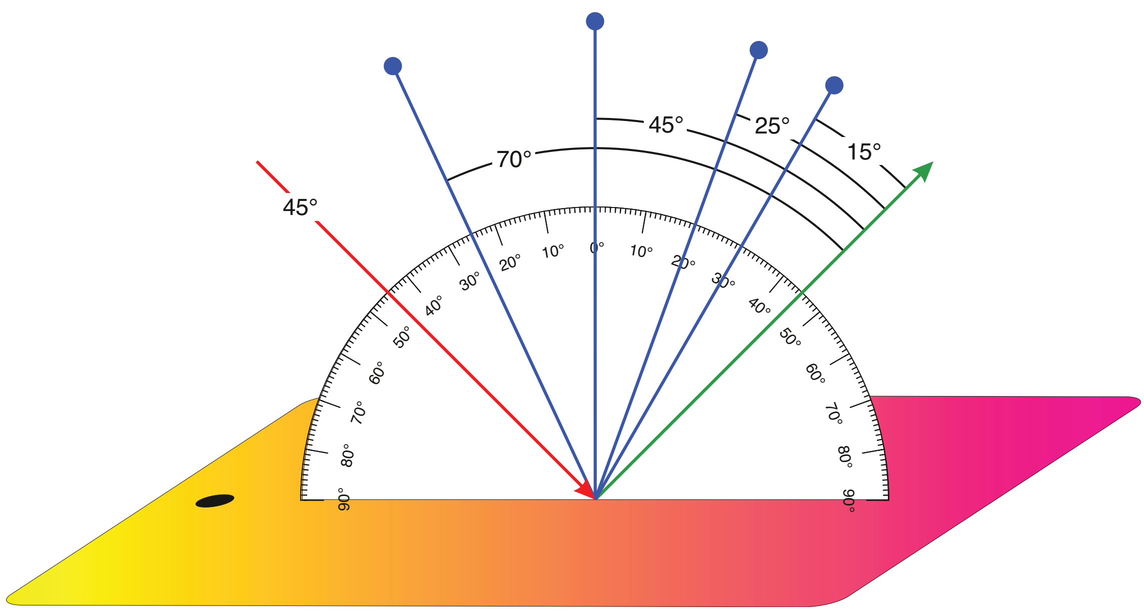

FIGURE 2 In 1995, the geometries still in use today were defined for fixed illumination at 45°

or attenuation of light waves. This gives rise to the typical resulting reflective color. A look at the interference law shows what this resulting interference color mainly depends on: first, the refractive index of the metal oxide; second, its layer thickness; and third, the angle of the incident light. The refractive index, like the layer thickness, is predetermined by the manufacture of the pigment. Depending on the layer thickness, the resulting color changes (Figure 4): A low layer thickness results in white interference pigments. If the layer thickness is increased, yellow, then red and blue, and finally green interference pigments are produced. The maxima of their reflection curves move from the ultraviolet to the visible range. It is important to note that white pigments are also interference pigments!

The third property, the dependence on the angle of the incident light, is a very important criterion for recognizing and characterizing interference pigments (Figure 5). Unfortunately, the manufacturers of measuring instruments have not recognized this criterion, although it has

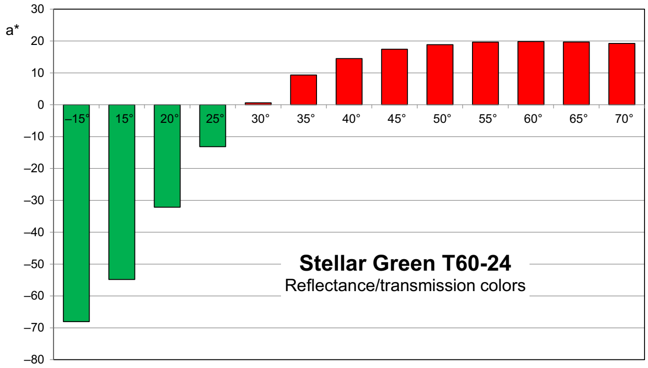

FIGURE 3 Colored transparent interference pigments with a titanium dioxide layer show a typical reflection color on their surface and the complementary transmission color on their underside. The change takes place in a transmission zone between 20° and 30° aspecular

FIGURE 4 As the thickness of the titanium dioxide layer increases, the resulting color changes from white to yellow, red and blue to green. The layer thickness is controlled by the wet chemical production process

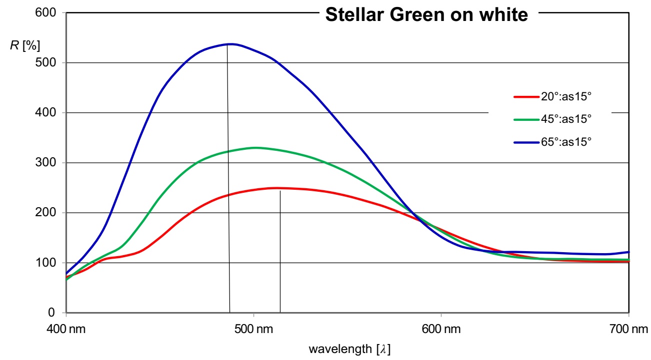

FIGURE 5 Typical of colored titanium dioxide interference pigments is the color shift when illuminated at a flatter angle for the same aspecular angle

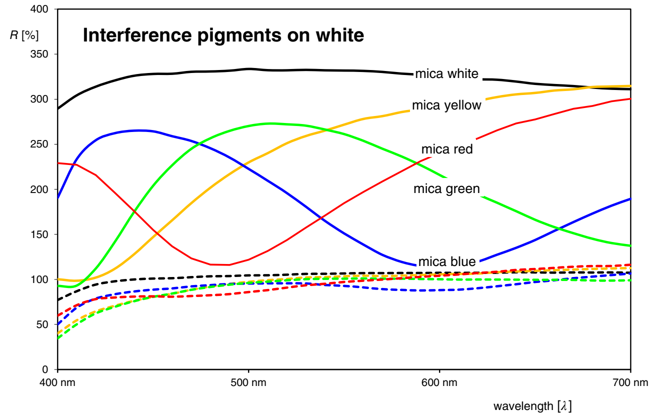

FIGURE 6 At 15° from gloss, these interference pigments show their typical reflections (solid lines). At 25° from gloss, that is, in the transition area, the reflections are almost the same (dashed lines)

been discussed again and again in the subcommittee. But it is also ignored in visual sampling. This leads to the discrepancy between the two methods. The crux of the matter lies in the different measurement geometries, which overall are not suitable for describing interference and which differ in visual sampling from those in instrumental sampling. And as long as samples with interference pigments are not compared with the same measuring conditions (= measuring geometries), discrepancies and differences in assessment will inevitably arise.

2 | MEASURING INSTRUMENTS

In the mid-1990s, the first portable measuring instrument came onto the market as a multiple-angle device. Before that, stationary instruments were already offered by ZEISS (GK311/M), where illumination and observation angles could be set independently.[2]

The portable instrument had an illumination angle of 45° and measured at 15°, 25°, 45°, 75°, and 110° from the specular. These angles were originally arbitrarily set but proved to be applicable and advantageous. The distances between these difference angles ("aspecular") are unequal and are 10°, 20°, 30°, and 35°. The instrument was built for automotive paints with aluminum pigments. However, it was also used to measure interference pigments because no other instrument was available.

After ASTM defined new geometries in 2008, portable instruments were offered with the additional difference angle of −15° from gloss (aspecular). This is in trans position, that is, on the side of the gloss angle opposite to the illumination angle. One instrument had additional illumination at 15°. It turns out to this day that most users of these instruments have little idea of the additional geometry, nor do they recognize its usefulness. In discussions with representatives of the paint and automotive industry, this is repeatedly stated and made clear.

Thus, the instruments have a fixed angle of illumination as well as various angles of observation, which also cannot be adjusted. In this respect, today's portable instruments are only conditionally suitable for measuring interference pigments. Thus, the possibility to detect the shift of the color of an interference pigment is missing. It can only be detected when the illumination angle is changed while the difference angle remains the same. White interference pigments do not show this shift, the measurements show clear differences to the colored interference pigments.

Colored interference pigments show their reflection color on the upper side and their transmission color on the lower side, which is complementary to the reflection color. If colored interference pigments are applied to a white background, the change from the reflection to the transmission color can be detected and measured. The reflection color can be seen up to about 20° from the gloss angle (Figure 6). This is followed by a transition area up to about 30° from the gloss angle, which is followed by the transmission color. However, common automotive paints have a rather low transparency, which is why this phenomenon does not appear with them. With them, the reflection color comes into play in any case. If, for example, the color of the blue interference pigment is not discernible in a mixture, its use would make no sense.[3]

3 | VISUAL ASSESSMENT

During visual assessment at the window or in the light booth, the laboratory technician first holds the painted panel or panels so that he can see the reflection of the window or lamp. Assuming an angle of illumination of 15° (with respect to the normal of the panel), one observes at the same angle (−15°). The angle between the illumination and the observation is therefore 30° (Figure 7). This angle does not change during the entire sampling when the sheet is moved up and down!

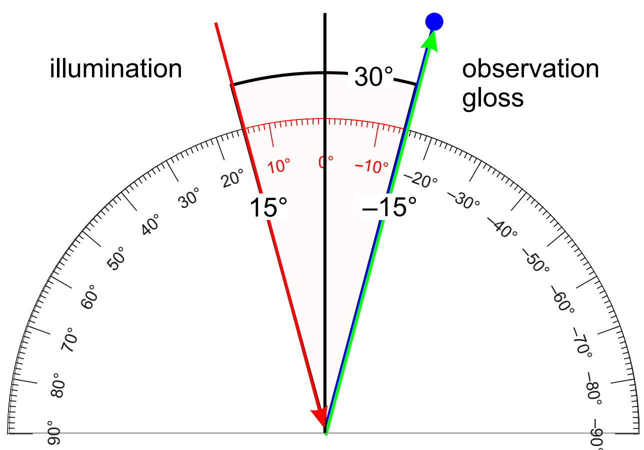

FIGURE 7 At the starting point, the panel is held so that it is illuminated at 15° and observed at −15° (in the gloss)

If the panel is moved downwards, the normal (perpendicular to the sheet) also moves downwards. And the illumination moves relative to the observer. At first, the angle between illumination and normal becomes smaller until the sample panel is illuminated at 0° in the normal (Figure 8). Then the illumination changes to the other side of the normal. And in the process, the position changes from trans to cis (Figure 9). Trans means that the observation is on the opposite side to the illumination

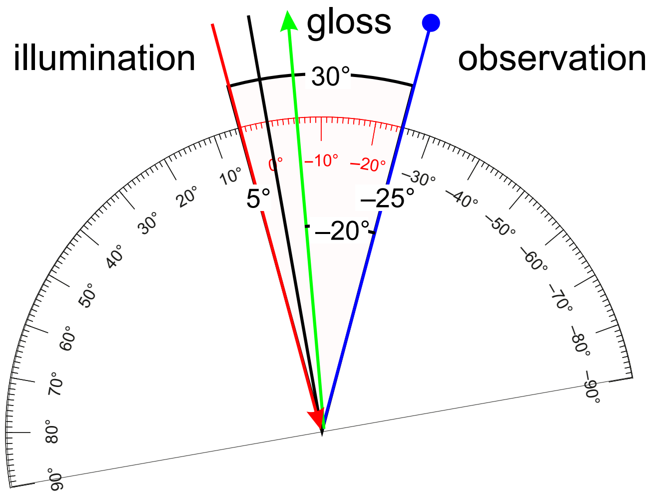

FIGURE 8 If the panel is tilted downwards, the normal also moves downwards and the illumination angle to the normal. The observation takes place in the trans area

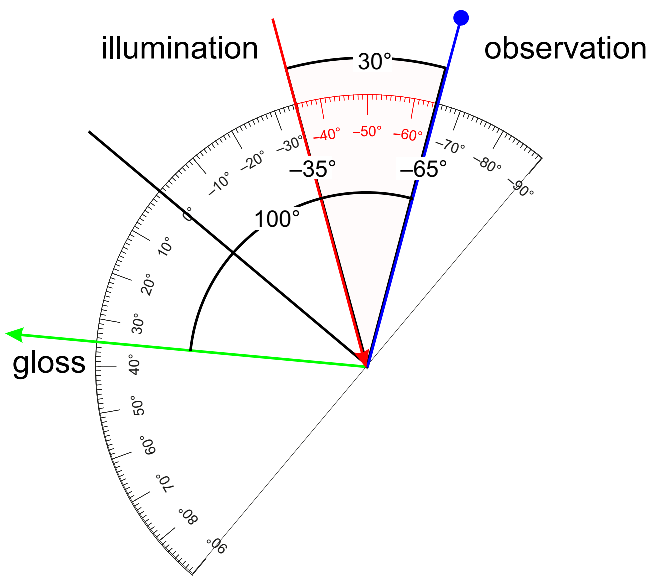

FIGURE 9 If the panel is tilted down further, the illumination changes sides to the normal. The aspecular angles become larger

to the specular angle. And cis are the observation angles between the specular angle and the illumination angle.[4]

If the panel is tilted upward, the normal also moves toward the observer (Figure 10). Thus, the illumination angle to the panel becomes larger, but the angle between illumination and observation always remains the same for all movements! The difference angle (aspecular) also becomes larger and larger.

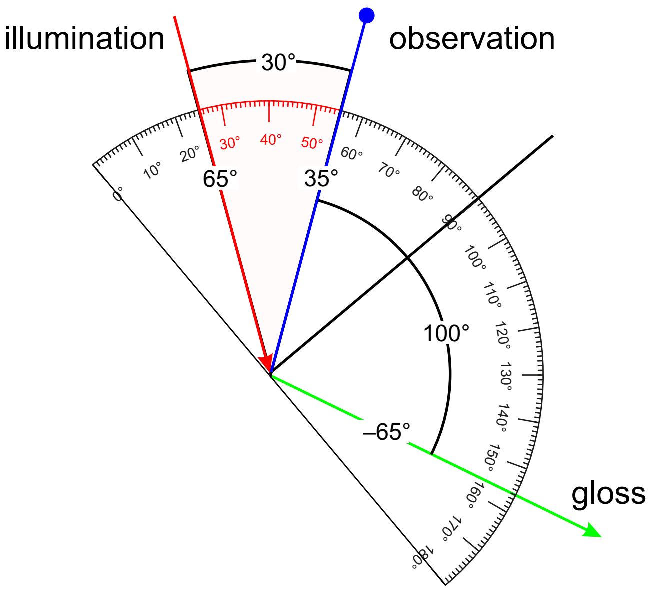

FIGURE 10 If the panel is tilted toward the observer, it moves toward him and the illumination angle increases

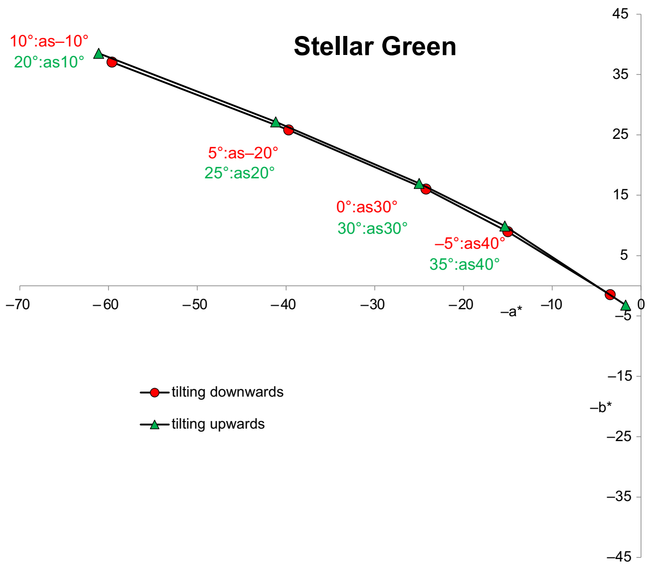

FIGURE 11 When tilting a sample sheet up and down at the window, the same geometries are adopted in each case. The color changes are the same

If one compares these geometries while observing the optical law of light inversion, one finds that the same geometries are assumed in each case when tilting up and down (Figure 11): For example, the geometry –20:as-50° (down) corresponds to the geometry 50°:as20° (up). In this respect, the same color shifts are observed when the

Tilting backwards

illumination [°]	Gloss [°]	observation [°]	aspecular [°]	Illu - Obs [°]	reverse_illu [°]	reverse_obs [°]
15	-15	-15	0	30	15	-15
10	-10	-20	-10	30	20	-10
5	-5	-25	-20	30	25	-5
0	0	-30	-30	30	30	0
-5	5	-35	40	30	35	5
-10	10	-40	50	30	40	10
-15	15	-45	60	30	45	15
-20	20	-50	70	30	50	20
-25	25	-55	80	30	55	25
-30	30	-60	90	30	60	30
-35	35	-65	100	30	65	35
-40	40	-70	110	30	70	40
-45	45	-75	120	30	75	45
-50	50	-80	130	30	80	50
-55	55	-85	140	30	85	55

Tilting upwards

illumination [°]	Gloss [°]	observation [°]	aspecular [°]	Illu - Obs [°]	reverse_illu [°]	reverse_obs [°]
15	-15	-15	0	30	15	-15
20	-20	-10	10	30	10	-20
25	-25	-5	20	30	5	-25
30	-30	0	30	30	0	-30
35	-35	5	40	30	-5	-35
40	-40	10	50	30	-10	-40
45	-45	15	60	30	-15	-45
50	-50	20	70	30	-20	-50
55	-55	25	80	30	-25	-55
60	-60	30	90	30	-30	-60
65	-65	35	100	30	-35	-65
70	-70	40	110	30	-40	-70
75	-75	45	120	30	-45	-75
80	-80	50	130	30	-50	-80
85	-85	55	140	30	-55	-85

FIGURE 12 The geometries correspond to tilting a panel with a starting point with illumination at 15° and observation at –15°. The angle between illumination and observation always remains 30°. The geometries resulting from reverse light are also shown

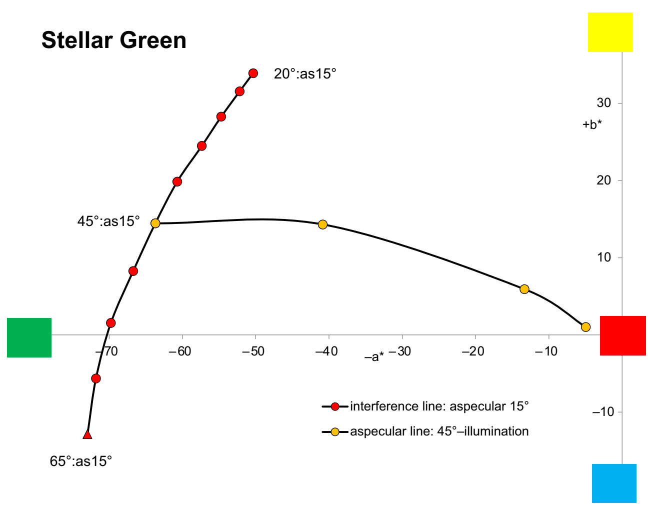

FIGURE 13 The interference line (different illumination angle with the same aspecular angle) and the aspecular line (fixed illumination with different aspecular angles) result in an anchor shape that is typical for this interference pigment. The interference line always points counter-clockwise

panel is tilted up or down. Most observers are not aware of this fact (Figure 12).

In overhead inspection, the observer stands with his back to the window and holds the sample panel or panels above his head. In this case, the panels face the window. If the panel or panels are moved up and down, geometries comparable to those described for the observation at the window are adopted. If the observation takes place in a light booth, the illumination is provided by a fixed lamp and the sample panel is moved up and down. This changes the angle of the illumination and the angle of the observation. Some instrument manufacturers now offer light booths in which the adjustable angles correspond to those of their measuring instruments. In this case, the illumination is coupled with a tiltable sample table.

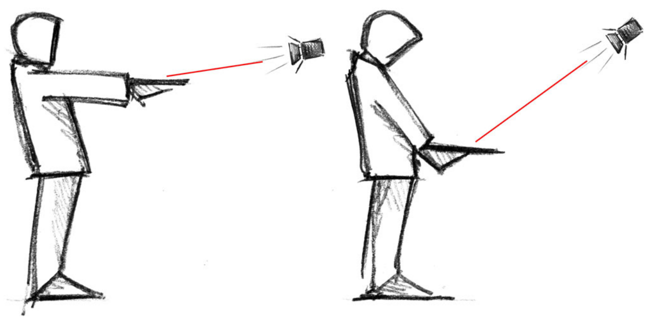

FIGURE 14 Interference can be observed when illuminating and observing flat with the arm outstretched and moving the panel parallel downwards to the steep illumination and observation

If one compares the geometries of visual assessment with those of instrumental assessment, no common geometries are found. As a result, discrepancies appear in assessment of interference pigments: The different geometries are also due to the fixed illumination angle of the measuring instruments. In visual assessment, this changes with each movement of the sample panel, just as the angle of observation changes at the same time.[5] The difference angle between the observer and the illumination source always remains the same for visual assessment at the window or in the light booth.

4 | COMPARISON

The color shift due to interference can be detected if the illumination angle is changed while the difference angle (aspecular) remains constant. Ideally, illumination is at a steep angle, the classic angle (45°) and a flat angle, and 15° of the specular angle (aspecular) is measured in each

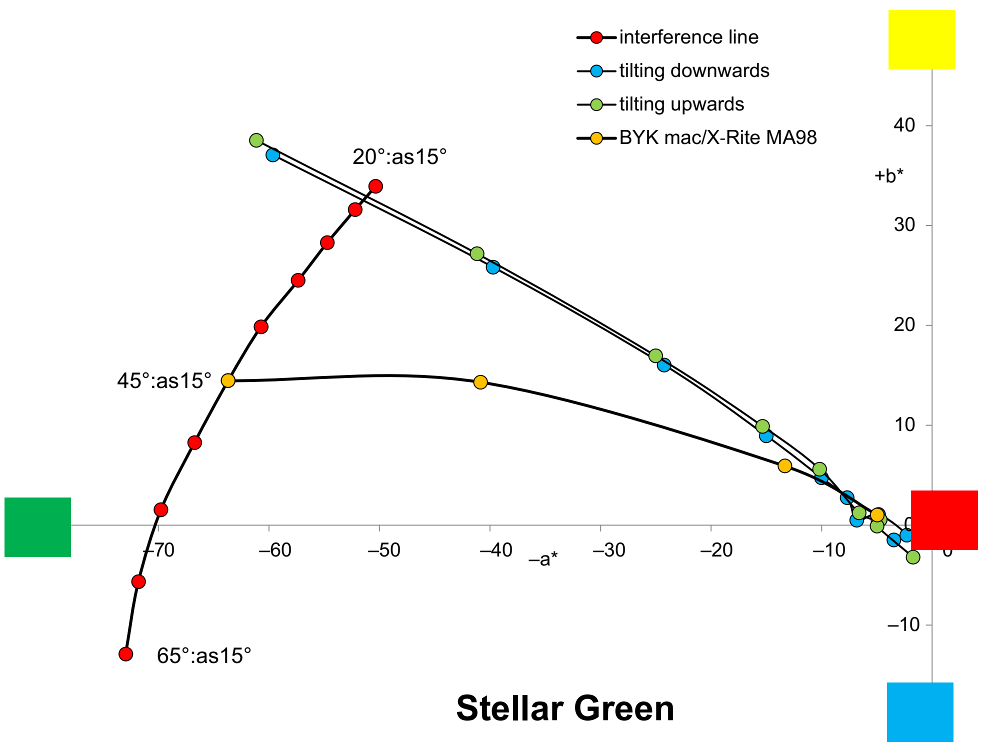

FIGURE 15 This chart shows the different methods: visually at the window, with portable measuring instruments and measuring the interference. The three results differ and cannot be compared

case. The measured values of these three geometries result in the typical interference line (Figure 13). It always runs counterclockwise, that is, the reflection curves shift to the shorter wavelength spectral range when the illumination is flatter.[6]

If one wants to reproduce these geometries visually, one holds the painted panel with an outstretched arm in the direction of a light source at approximately the same height. While doing so, the sheet is illuminated flat and observed near the gloss. Then one moves the sheet parallel downward, illuminating the sheet steeply. This movement traverses all illumination angles from flat to steep (Figure 14).

Although the illumination angle changes and the difference angle remains the same during this parallel movement, both the illumination angle and the difference angle change during conventional visual assessment when a panel is moved up and down. This does not observe the interference colors that require different illumination angles with the same difference angle.

Since the current instruments illuminate the sample panels with the illumination angle fixed, they also cannot detect the interference. With a measuring instrument with second illumination, the interference line can be reproduced. In addition to the two geometries 15°/as15° and 45°/as15° as steep and classical illumination angles, the geometry 45°/as-15° can also be used as a flat

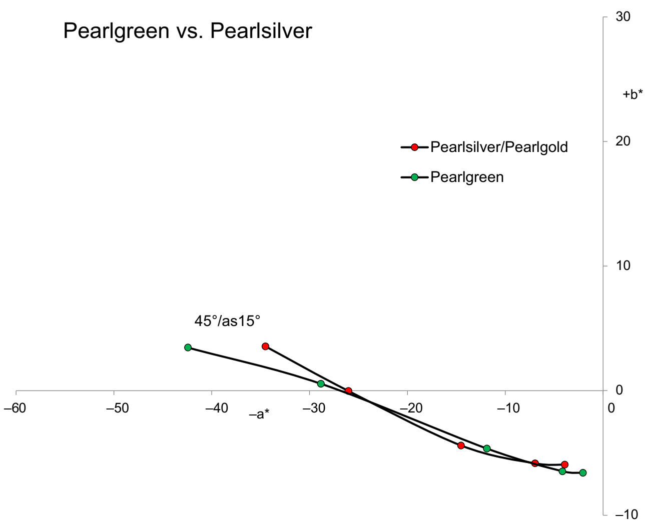

FIGURE 16 The same OEM color Dragongreen was pigmented twice differently: once with mica green and once with mica white. Since the interference lines, which clearly show the difference, were not measured, both lots were accepted

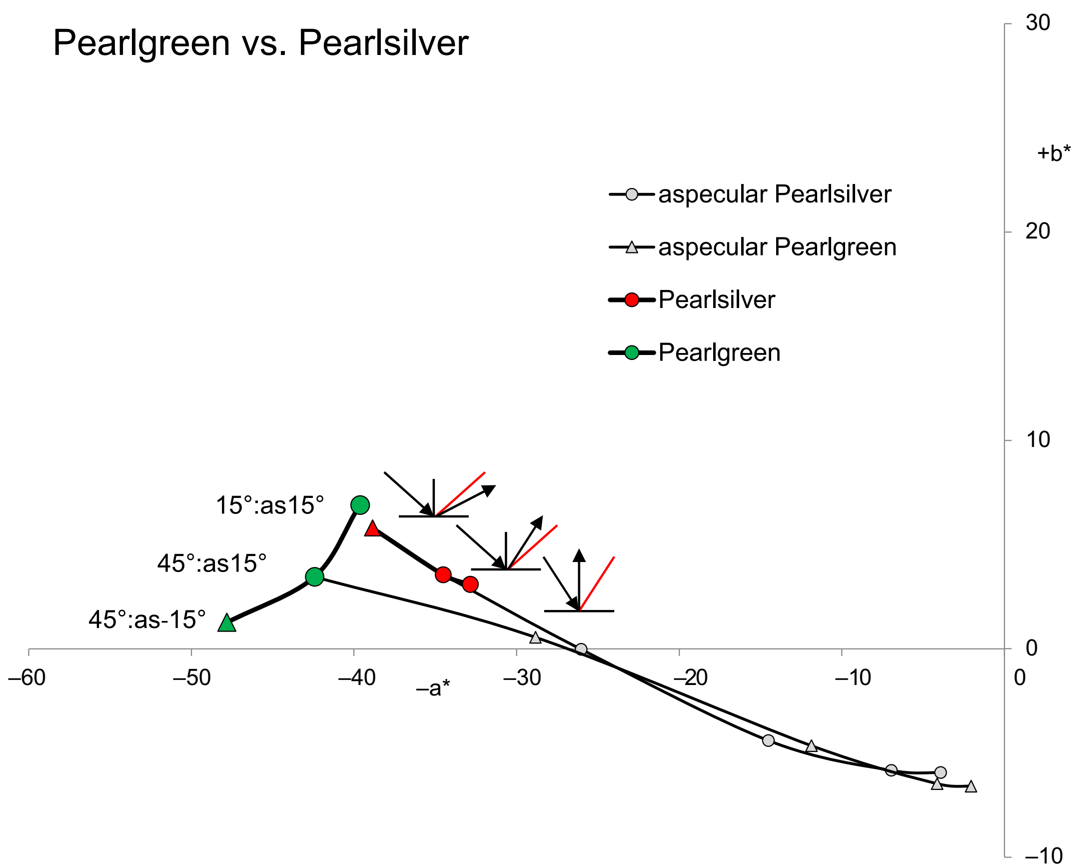

FIGURE 17 Measuring the interference, the difference between the lot with Pearlgreen and the lot with Pearlsilver is obvious

illumination geometry. Due to the law of light reverse, 45°/as-15° corresponds to the geometry 60°/as15°. With the measured values of these geometries, the interference line is obtained which represents the color shift of the interference. As mentioned, it always runs counterclockwise (Figure 15). Together with the aspecular line, it forms an anchor shape that can be used to identify any colored interference pigment.[7]

This anchor shape also remains in mixtures with colored pigments, which is why interference pigments can also be identified in mixtures. The anchor shape is typical and does not change in different application media: a blue interference pigment does not appear red if it is used in plastic instead of in a paint application.

White interference pigments, which are very commonly used in automotive coatings, form an interference line that is an extension of the aspecular line and does not bend counterclockwise due to the lack of color shift (Figures 16 and 17). If the reflectance curves of white interference pigments or mixtures with colored pigments are observed, they increase when the illumination is flatter. This behavior is comparable with aluminum pigments or corresponding mixtures. For more precise identification, a microscope can be used to distinguish aluminum pigments easily from interference pigments.[8]

The measurement geometries of current portable instruments are not suitable for adequate measurement of interference pigments. The same applies to conventional visual assessment. As long as the user is not aware of which measurement geometries are used in visual and instrumental assessment, discrepancies between the two methods keep appearing. It would be important to have instruments that can detect interference. This is because the number of automotive coatings with interference pigments will continue to increase in the coming years. However, the user is dependent on what the manufacturers of the measuring instruments have to offer, because he cannot configure a suitable instrument. The manufacturers of automotive refinish paints offer comprehensive formulation systems and use measuring instruments for this purpose. However, these are used to search in existing formulation databases.

For successful assessment, it is necessary to know the optical properties of the interference pigments and the corresponding geometries for assessment. This is the only way to understand the discrepancies between visual and instrumental assessment. It would also help to solve the discrepancies if the instrument manufacturers would deal with the issue of interference more intensively and adapt their instruments.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Werner Rudolf Cramer studied industrial chemistry at the Westfaelische Wilhelms-Universitaet, Münster, Germany. During his studies, he also worked on the development of new penicillins and with the application of liquid crystals. After his study, he started as a freelancer and developed ideas for automotive color design in cooperation with Volkswagen, MAN (trucks), and Ford. After many years, he switched to more scientific work and dealt more deeply with interference pigments and their color measurement. The close cooperation with Zeiss and Merck led to the development of the multiangle instrument GK311/M. Since 1999, he was engaged in ASTM and DIN to define new method to measure interference pigments. He has intensified his cooperation with car, paint, and pigment manufacturers in recent years. Over 800 publications have appeared in magazines worldwide as well as in various books. This also includes presentations. Publications released from 2012 onwards can be downloaded free of charge from his website www.wrcramer.de (English, Chinese, and German).

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