MEASURING SPECIAL EFFECTS

A Comparison of Various Spectrophotometers

Many industries, notably the automotive, printing, plastics and cosmetics industries, would not be what they are today if it were not for special-effect pigments. At one time the first-generation classic effect pigments were all the rage, but now designers and stylists are crying out for the latest special-effect pigments. The new generation of effect pigments requires a totally different system of measurement and characterization. The capabilities of the various spectrophotometers available for this purpose are discussed in the context of these special-effect pigments.

Special-Effect Pigments — Color and Perception

Historically, conventional aluminum and bronze pigments were succeeded by so-called nacreous or pearlescent pigments, which are mica-based. The principle distinguishing features of the latest generation of effect pigments are provided by the physical nature and the structure of the pigment particles. These pigments consist essentially of coated silica or aluminum flakes, ultrathin multilayers or liquid crystals in organically crosslinked polymers.[1]

The pigments can be roughly categorized as follows.

- Metallic pigments consist of very thin metallic flakes or wafers that act as miniature mirrors. Their intensity changes according to the angle from which they are viewed. Maximum light intensity is achieved near the "gloss", the angle at which the incident light is reflected. Minimum is experienced at an angle far away from the gloss.

Figure 1 / Interference Shift Caused by Keeping the Aspecular Angle Constant at 15° and Varying the Illumination Angle

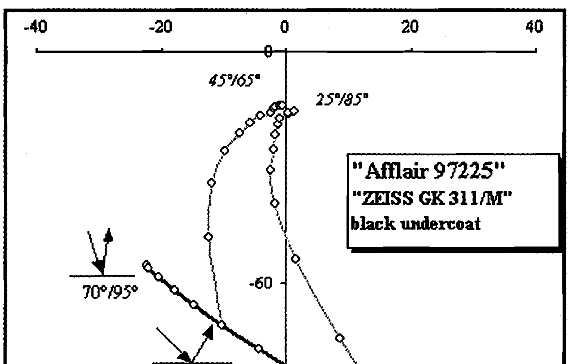
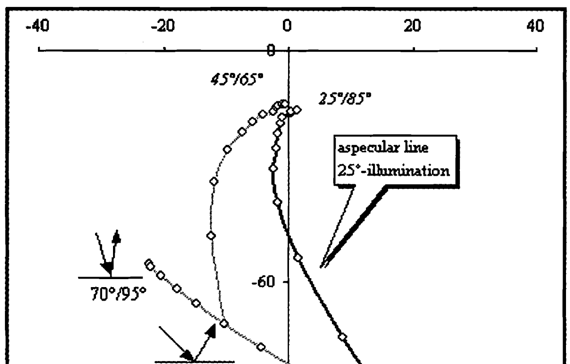


Figure 2 / Shift Caused by Keeping the Illumination Angle Constant at 45° and Varying the Aspecular Angle



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Factors affecting this flip-flop effect are the shape and size of the pigment particles and the way they are laid down within the paint.[2,3]

- The most requested class of effect pigments at the moment is basically a mica flake coated with single or multiple thin layers of metal oxide. The interplay of colors produced by these pigments is due to the layered structure of the metal oxide, which is also responsible for the rich deep glossy effect.[2,3]
- Striking optical effects are achieved by combining specially selected coated transparent flakes of silica. The flakes are produced in a uniform thickness, which gives purer interference colors and gloss. Brightness of color and a conspicuously angle-dependent viewing effect provides outstanding styling potential.[3-5]
- Coated aluminum-oxide flake pigments offer a brilliant sparkling effect, a phenomenon previously unseen in pigments of such small particle size.[3-5]
- Opaque multiple-layer pigments produce rich interference colors that depend strongly on the viewing angle.[6,7]
- The optical effects of liquid crystals are due to the helical structure exhibited by highly crosslinked liquid-crystalline structures of organic molecules. The pigments are transparent and produce their angle-dependent effects on colored undercoats.[8,9]

Interference — Color by Physics

Although there are many marked differences in the way modern effect pigments are made, their optical properties can all be explained in terms of interference.[10,11]

Light impinging on a pigment is partly reflected from its surface and partly refracted through it. This causes wavelength shifts, with individual rays of light intermingling and so causing the familiar interference. When wave crest meets wave crest, the amplitude becomes more intense. A wave trough meeting a peak partially cancels the amplitude, though total cancellation practically never occurs.

As an example, a classical interference pigment such as an Affair type pigment consists of a flake of mica surrounded by a layer of titanium dioxide. When white light falls on this type of pigment, some of it is reflected at the surface of the pigment, also creating a phase shift of half a wavelength. The remainder of the white light is transmitted through the titanium dioxide layer and meets the surface of the mica, where it is again partially reflected. This reflected component emerges from the pigment parallel to the first reflected component. Since it had further to travel through the titanium dioxide layer, the wavelengths of the second light component will be back in phase with those of the first. As a consequence, the light waves will be intensified and thereby produce the color reactions as perceived by the human eye. By calculating the shift under simple and ideal conditions, it is possible to arrive at an equation for maximum reflection and hence also for the resulting color. The elements of this equation are the thickness of the refracting titanium dioxide layer, its refractive index and the angle of illumination. As the thickness of the layer increases, the color of the Afflair pigment changes from silver-white, through yellow, red and blue, to green.

> Light impinging on a pigment is partly reflected from its surface and partly refracted through it.

Starting from a flat angle of incident light (relative to the horizontal surface of a test panel), the maximum shifts to the longer-wave region as the angle of illumination becomes steeper. For example, Blue Pearl changes from violet to greenish blue as the angle is altered from flat to steep (see Figure 1).[12] Such color shifts are indicative of interference phenomena at work[13,16,17] and are thus typical of these kinds of pigment. If the illumination angle is kept constant and the viewing angle altered, again a color shift is perceived (see Figure 2). Applying the aforementioned interference pigments to a white undercoat will, at more than 30° from the gloss angle, produce the color that is complementary to the immediately reflected color as it is reflected from the white undercoat (see Figure 3).

Two fundamental color shifts can be discerned in interference pigments.

- The first is the shift produced by varying the illumination angle and keeping the aspecular angle constant (i.e., 15° from the gloss angle). This is the typical interference shift.
- The second effect is when the illumination angle is kept constant (i.e., at 25° or 45°) and the aspecular angle is varied. In this case (depending on the illumination angle), the typical color curves are pro-

duced which, as the viewing angle increases, tend towards the same or almost the same point. This phenomenon is known as aspecular shift.[17]

Visual Judgement of Effect Pigments

Since these two types of shifts are particularly spectacular in the new-generation pigments, new criteria must be set for their visual judgement. Typically, visual judgement involves tilting the sample panel backwards and forwards to produce a shift. However, this tilting simply simulates changes from a fixed light source and does not account for color shifts produced through interference. It simply mimics the classical way of testing metallics. To allow interference shifts to be observed, the panel must be moved so as to allow the angle to the light source to be made steeper or flatter (see Figure 4).[1]

A real object, such as an automobile, has numerous angles and contours. When the sun is high in the sky, horizontal surfaces reflect directly upwards; the observer sees the effect away from the gloss. It is interesting to note that different color effects are produced depending on whether the observer is standing on the side of the gloss nearest to the light source in the cis position or "behind the gloss" in the trans position (see Figure 5).

With the sun in the high position, light rays strike the sides of the automobile at a shallow angle and the viewpoint is a long way away from the gloss. When the sun is low in the sky, on the other hand, light impinges on the sides of the vehicle at a steep angle; at the same time, horizontal surfaces such as the roof and hood are illuminated from a flat angle. Again, a variety of color effects are achieved depending on how tall the observer is and how far he/she is away from the automobile.

Multi-Angle Measurements — Absolutely Essential

All possible colors and color shifts must be used to judge and define the pigments. Studies show the measuring geometries of the day to have been generally adequate for the first-generation effect pigments;[14] nevertheless, there were a small number of problem pigments that were not amenable to spectrophotometric testing.[15] For the modern, second-generation effect pigments, extensive angle-dependent spectrophotometric testing is a necessity.[16-18]

The immediate question is: what features must the spectrophotometer have to enable this type of testing to be carried out? The answer to this question can be derived from points previously made. First, there must be a variable light source. In a spectrophotometer this is achieved through pre-set angles. Second, the observation point must also be variable. This is again achieved through pre-set angles.

This is the most efficient way of measuring the color dynamics that result from the combination of geometries and pigments.

Figure 3 / Shift Caused by Keeping the Illumination Constant at 25° and Varying the Aspecular Angle

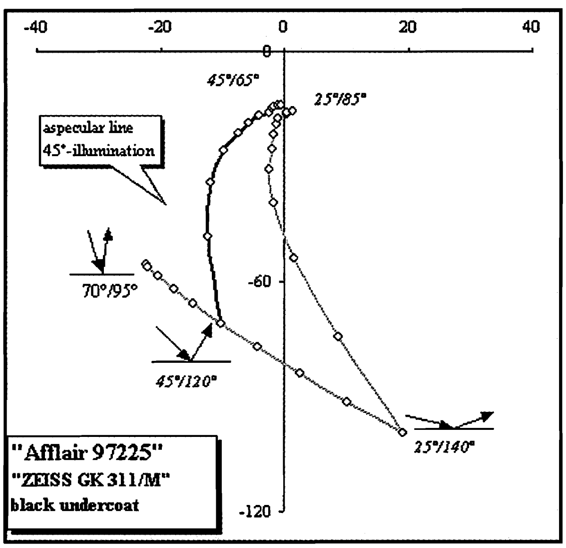


Figure 4 / Different Ways of Visually Judging Effect Pigments

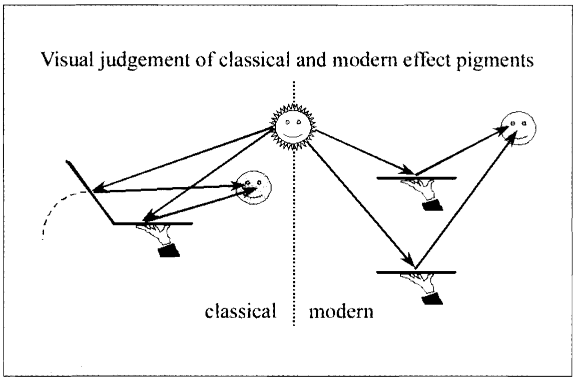
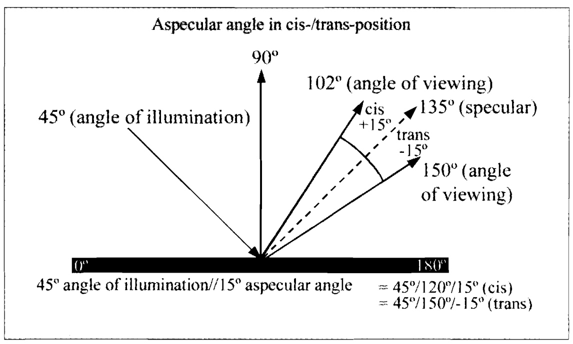


Figure 5 / Possible Viewing Angles Relative to the "Gloss"



Spectrophotometers – An Angle-Dependent Overview

Various companies produce angle-dependent spectrophotometers. The GretagMacbeth Auto-Eye 642 illuminates the surface from an angle of 45° and offers viewing angles of 25°, 45°, 75° and 110° (aspecular angles). The X-Rite MA68II, too, illuminates at 45°; in this instrument the viewing angles are 15°, 25°, 45°, 75° and 110° from gloss. With their fixed angle of illumination and their optional viewing angles, the two instruments are very similar. The Minolta and Optronik spectrophotometers, however, illuminate at various angles and measure at a single, fixed angle. With an observer of 0°, the Minolta CM-512m3 measures under 25°, 45° and 75° circular illumination; the Optronik MultiFlash measures at 45° under illumination in eight geometries ranging from 25° to 115°. The effect angle in the latter case changes from the trans to the cis position within the geometric series.

The Phyma WICO 5&5 System measures under 22.5° and 45° illumination, offering 67.5°, 0°, -22.5°, -45° and -67.5° viewing and a large measuring spot. The five presets between 0° and 180° (relative to the horizontal) provide virtually ideal pigment definition.

The Murakami GCMS-3 provides complete definition in 1° steps. The instrument features illumination from 16° to 180° and observation up to 196° (transmission). Totally variable reflectance and transmittance measurements from 0° to 360° can be achieved with the GON 360 from Instrument Systems.

For comparison of results, the Zeiss GK 311/M multi-angle instrument was used, though the instrument is no longer manufactured. In it, it is possible to set both the angle of illumination and the viewing angle independently of one another in 5° steps. The minimum illumination angle is 25° (horizontal) and the maximum viewing angle 155°.

The Results – More than Just Numbers

The effect pigments were incorporated in 3% concentration into NC lacquer and machine-applied to black-and-white cards. These results refer to pigments over a black undercoat. For greater clarity and comparability, all angles quoted are relative to the sample horizontal.

Afflair 97225 Ultra Blue Pearl

This transparent pigment is one of the most frequently used blue pigments. Its powerful blue reflection color changes from blue-violet when illuminated at a flat angle to blue-green when the angle is steeper and when viewed near the gloss. Moving from "near gloss" to "remote from gloss" causes the color to become duller irrespective of the angle of illumination. The Zeiss GK 311/M clearly shows this color change — as an interference shift as the angle of illumination is varied from 25° to 70°, and as aspecular shift at 25° and 45° illumination as the effect angle rises above 15°. The angles change clockwise from 0° to 180°relative to the horizontal. The 45° illumination angle has its equivalent specular angle at 135°; measurement with a 15° effect angle thus occurs at 120°.

Figure 6 / The Same Effect Angle Can Thus Be Based on Various Measuring Geometries and Thus Describe Different Color Sites

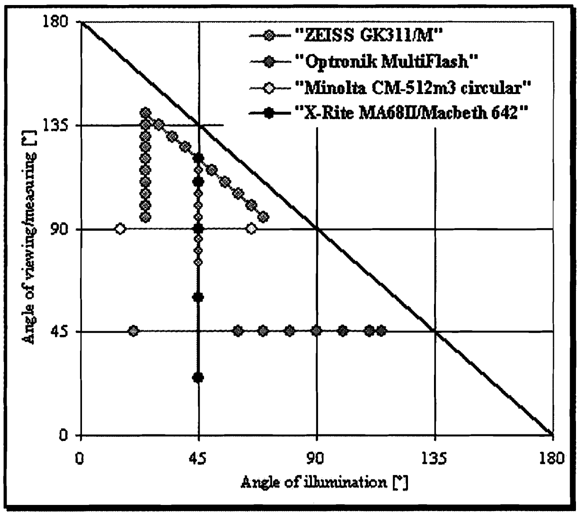
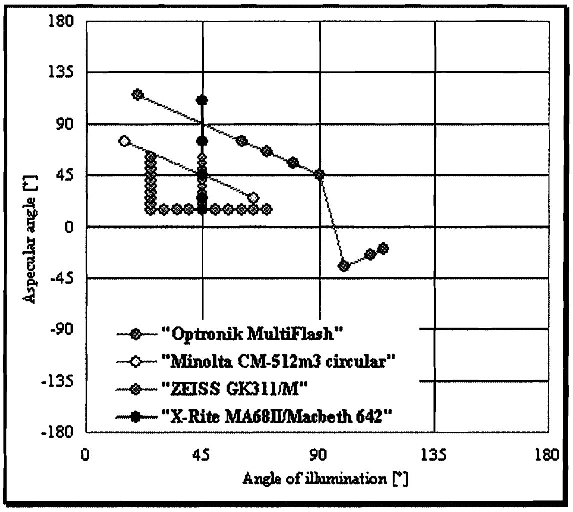


Figure 7 / Schematic Comparison of the Geometries of Various Measuring Systems: The Zeiss GK 311/M Measures Under Constant Illumination or a Constant Aspecular Angle. The X-Rite and Macbeth Instruments Measure Under Constant Illumination; the Optronik MultiFlash Measures from a Constant Viewing Angle under Various Illumination Angles, the Effect Angle Being Cis or Trans to the Specular Angle



The 45° effect line (aspecular shift) for Afflair 97225 can be demonstrated in the X-Rite MA68II beginning with 15° up to a 110°effect angle. The Macbeth 642 gives similar results, except that it only begins measuring at a 25° effect angle. The Optronik MultiFlash, too, only starts at a 25° effect angle, though comparison is difficult as the measuring geometrics change from the cis to the trans position. Conspicuous during measurement of the transparent pigment types is their "swing" to the 115° geometry. With its circular illumination, the Minolta CM512m3 can barely produce the full color effects of Afflair 97225, having, as it does, only three measuring geometries (see Figure 8).

Colorstream Ti-Pigment

This pigment is one of the second-generation innovative types based on thin flakes of silica (SiO_2). The color changes from violet to green at a constant effect angle of 15°. The effect lines (aspecular shift) under 25° and 45° illumination are tending toward the same point.

It can be clearly seen that the aspecular shift at 45° shows good agreement in both instruments (see Figure 5a). However, it also becomes clear that the instrument with the fixed illumination angle of 45° cannot adequately display the broad color bandwidth of the pigment.

ChromaFlair 190

This pigment changes from yellow to green via red, violet and blue when the angle of illumination is changed while the aspecular angle is kept constant. When the illumination angle is kept constant, the color changes to dull.

The area that is described by the color changes can be well presented in the a*b* diagram. Although the CIELAB system, strictly speaking, is only applicable for showing color differences, it is nevertheless useful for demonstrating color effects. The Zeiss GK 311/M cannot clearly register visual impressions of color. Since its design does not permit illumination angles flatter than 25°, the visual impression of yellow at < 25° can no longer be measured.

While all of the measuring instruments register the color change at 45° illumination or observation in more or less the same way, the positions of the data points with the Minolta are much more conspicuous here than with Afflair 97225. This instrument changes the angle of illumination and the aspecular angle simultaneously, as shown in Figure 10.

Magic Purple ED 1480

BASF's Variocrom pigments are comparable with the ChromaFlair pigments from Flex Products. Starting with yellowish-red, the color of this pigment shifts toward red-violet when the angle of illumination is made steeper while the aspecular angle is kept constant. Under constant 25° illumination the effect line (aspecular shift) at 30° from gloss intersects the interference line (interference shift) at geometry 35°/130° and forms a common point of different intensities.

Clearly to be seen with this pigment is the similarity of measurement data obtained with the various instruments, though the Minolta does stand out on account of its different measuring geometrics. Also, the Optronik MultiFlash using flat illumination far exceeds the results of the other instruments.

Figure 8 / Interference and Aspecular Shift for Afflair 97225 in the a*b* Diagram of Various Measuring Instruments

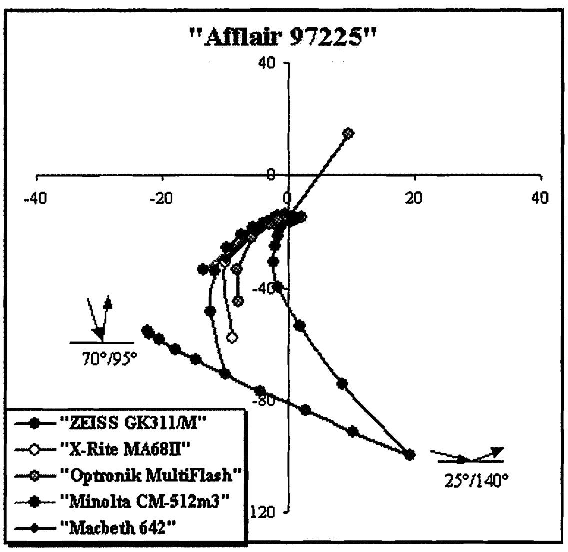
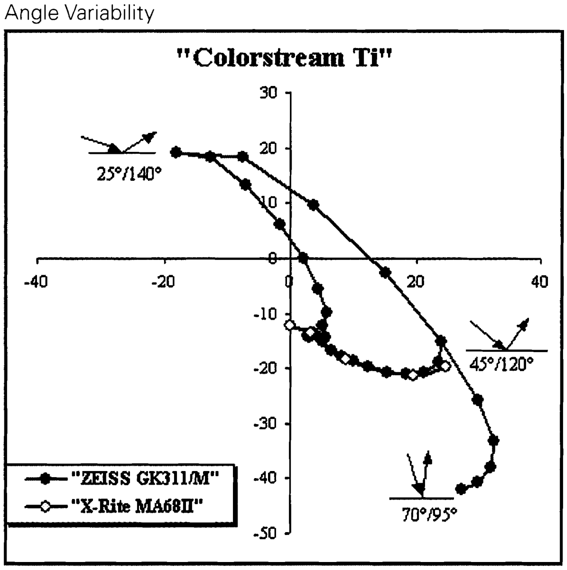


Figure 9 / Comparison between the Measurement Data of Two Spectrophotometers With and Without Illumination Angle Variability



Helicone 624

Visually, an intense green is observed with flat illumination, changing to an intense red as the angle of illumination becomes steeper. Changing the observation angle away from the gloss causes this pigment to tend toward dull.

The Zeiss GK 311/M produces an interference line with pronounced arc shapes with yellow as transition color in the region of 45° illumination, while the other instruments only "begin" with yellow and give measurement data tending toward dull as the aspecular angle increases.

The Issues – and a Pragmatic Solution

The measurement data show that the visual behavior of the second-generation effect pigments cannot, or can only barely, be measured using the spectrophotometers presently available. The new DIN 6157-2 standard goes as far as to exclude these pigments. Only two manufacturers offer flexible goniospectrometers that are suit-

Figure 10 / Interference and Aspecular Shift for a Multi-Layer Effect Pigment in the a*b* Diagram of Various Measuring Instruments

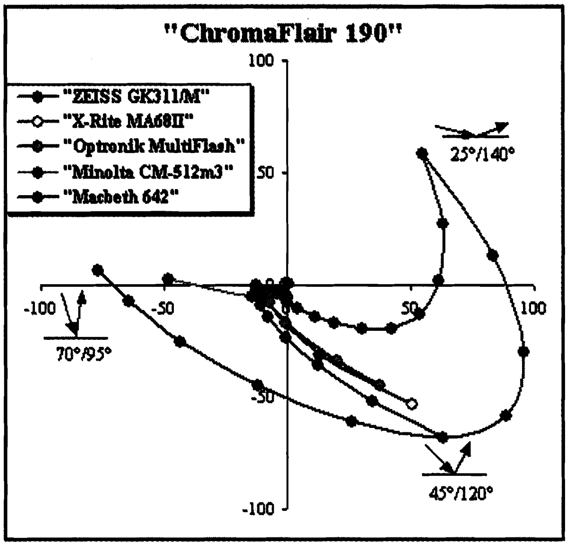


Figure 11 / Interference and Aspecular Shift for a Multi-Layer Effect Pigment in the a*b* Diagram of Various Measuring Instruments

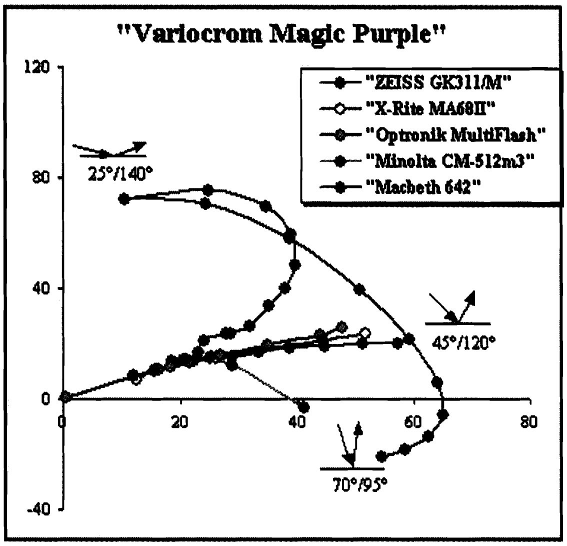


Figure 12 / Interference and Aspecular Shift for a Liquid Crystal Effect Pigment in the a*b* Diagram of Various Measuring Instruments

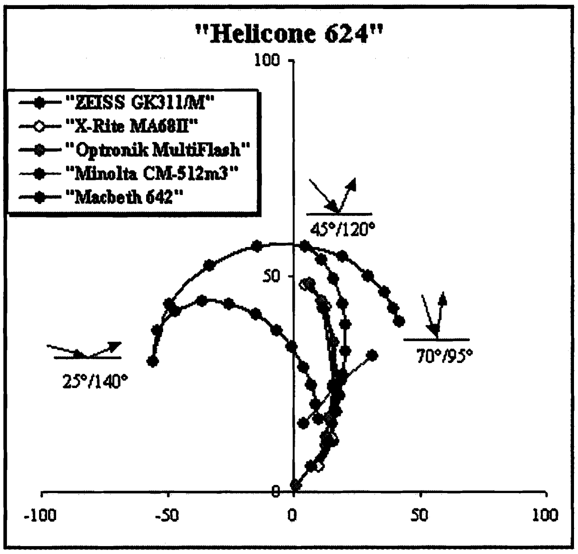
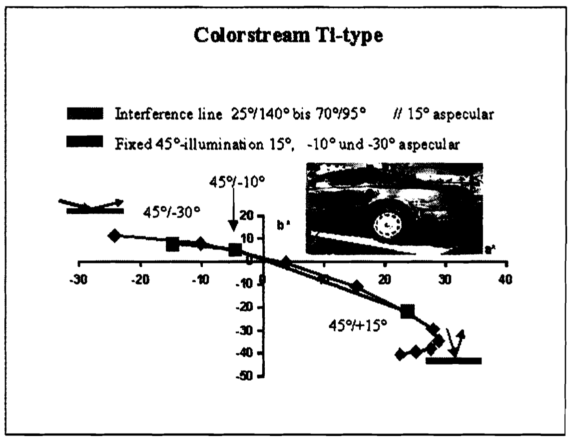


Figure 13 / Comparison of Interference Shift under Various Illumination Angles and a Constant 15° Aspecular Angle and under Constant 45° Illumination and Various Cis-Trans Effect Angles



Interference effect pigments exhibit color changes that can be portrayed two-dimensionally in the a*b* diagram by plotting aspecular and interference shift.

able for R & D. On the production floor there is a need for portable instruments having more measuring geometries than the instruments presently available. As an interim step in the existing systems with 45° illumination, it might be possible to introduce a measuring angle behind the gloss or trans angle. Extensive experimental measurements add support to this notion (see Figure 13).[1]

Summary

Interference effect pigments exhibit color changes that can be portrayed two-dimensionally in the a*b* diagram by plotting aspecular and interference shift. Keeping the aspecular angle constant leads to interference shift as the angle of illumination is altered. Aspecular shift is the result of illuminating from a constant angle and varying the angle of observation.

Therefore, any measuring instrument used must be able to measure both these types of shift. Only then will judgement of the pigment be optimum and precise. Illumination and observation angles should therefore be introduced as close as possible to the horizontal, so as to better mimic the actual visual impression through the measurement data.

Acknowledgement

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