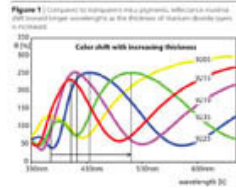


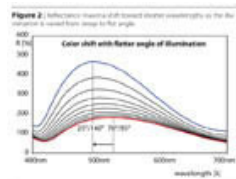
# Interference Pigments

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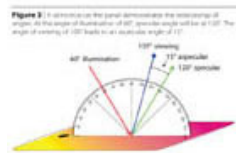


Interference pigments are employed in many automotive and industrial paint formulations. Their high popularity is due to their fascinating interplay of color and to effects due to the various materials employed in their layered structures. Refractions and reflections of light at, and within, those layers cause interferences yielding selected colors.



## Classification

Interference pigments may be classified by either the method employed for their manufacture or by their structure. Substances, such as titanium dioxide or iron oxide, that have high indices of refraction, may, for example, be deposited on a transparent substrate, such as mica in the case of Iridodin, silicon dioxide in the case of Colorstream, or aluminum oxide in the case of Xirallic. Such pigments are produced using wet-chemical processes, while those having an aluminum layer as an internal reflector (Variochrom, ChromaFlair and SpectraFlair) are manufactured in high vacuum. Liquid crystals are also classed as interference pigments.



Although development work on interference pigments has led to significant advances over recent years, progress in the areas of visual and instrumental methods for their characterization and testing methods has failed to keep pace with those advances. Among the reasons for that failure are insufficient effort devoted to their optical properties and the lack of suitable metrological instrumentation.

Table 1: The table gives an overview of the differences that arise in the case of these common setups of the measurement geometry for different angles of illumination. The comparative appearance in the result of varying angles of illumination is shown in the respective column of the corresponding color.

Illumination [°]	Specular [°]	Viewing [°]	Angular [°]	Info
45	135	135	15	ca
45	135	135	20	ca
45	135	90	45	ca
45	135	90	75	ca
45	135	25	110	ca
135	45	45	15	spec
135	45	45	20	spec
90	90	45	45	spec
90	90	45	75	ca
25	135	45	110	ca

## Angular Relationships of Metrological Setups

Interference pigments manipulate incident light by means of refractions and reflections such that the resultant refracted and reflected light generates color perceptions in the human eye and brain. That refracted and reflected light is selectively affected by two major factors. First, the thicknesses of their layers and the materials constituting the latter determine their “base colors”. For example, depositing layers of titanium dioxide having different thicknesses on a mica plate yields silvery-white, yellow, red, blue or green.

The reflectance curves of such pigments for a particular geometry, e.g., 45°/120° (illumination/observing), exhibit a readily

discernible shift in their respective reflectance maxima toward longer wavelengths. The reflectance minimum of the silvery-white pigment will be shifted from the UV to the blue spectral range as layer thicknesses increase, while, in this particular case, the plateau of its reflectance maximum spans the green, yellow and red spectral ranges and leads to a gold-yellow color. Further increases in layer thickness will shift that plateau toward even longer wavelengths, and simultaneously shift the next reflectance maximum from the UV to the blue-violet spectral range. The latter maximum will then be responsible for its blue color, as well as the green color that arises when the thickness of its layers is further increased, when viewed at the angle of specular reflection. The ostensibly unusual ordering, yellow, red, blue and green, of colors for increasing thickness of the layers of titanium dioxide is thus due to its reflectance maxima being shifted toward longer wavelengths. (Figure 1)

The second factor involved is attributable to one of the key features of interference pigments. Optic laws dictate that their reflectance maximum will be shifted toward shorter wavelengths as the angle of illumination is varied from steep, near-normal incidence to flat, near-grazing incidence. That key feature is peculiar to the particular pigment involved, and thus may be used for its characterization and identification. (Figure 2)

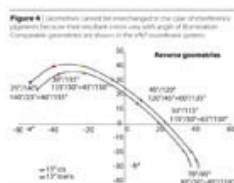
If these particular optical properties of interference pigments are to be utilized for their visual and instrumental assessment, the first thing that will be necessary is to address the matter of geometries to be employed. If a semicircle graduated from  $0^\circ$  to  $180^\circ$  inclusive, is set upright on the test panel, practical considerations dictate that the angle of illumination should range from  $0^\circ$  to  $90^\circ$  and that the associated angles of specular reflection should range from  $90^\circ$  to  $180^\circ$ . For example, if the angle of illumination is  $60^\circ$ , the angle of specular reflection will be  $120^\circ$ , i.e., the angles of illumination and specular reflection will be displaced  $+30^\circ$  and  $-30^\circ$  from the local normal to the surface, respectively. Since measurements will be made at angles differing from the angle of specular reflection, another factor needed for specifying the geometries involved will be the aspecular angle, i.e., the difference between the angle of specular reflection and the angle of observation. For example, if, in the case of the example mentioned above, measurements are made at  $105^\circ$ , the aspecular angle will be  $15^\circ$ . (Figure 3)

The resultant colors exhibited by interference pigments vary with the geometries involved, which is why accurate definitions of, and accurate statements respecting, the latter are essential. Defining the angles involved utilizing the semicircle method will greatly simplify comprehension of particular situations. Although stating the angles of illumination and observation as  $45^\circ$  and  $120^\circ$ , respectively, is unambiguous, an aspecular angle of  $15^\circ$  may occur for various angles of illumination, which is why one should not allow themselves to become confused by statements confined to the difference in the angles of specular reflection and observation.

Two examples will indicate that comparable angular relationships will not necessarily occur in such cases. In the case of the first example, measurements are made at  $120^\circ$ ,  $110^\circ$ ,  $90^\circ$ ,  $60^\circ$  and  $25^\circ$  for a constant  $45^\circ$  angle of illumination. The respective aspecular angles involved will then be  $15^\circ$ ,  $25^\circ$ ,  $45^\circ$ ,  $75^\circ$  and  $110^\circ$ , referred to the  $135^\circ$  angle of specular reflection. In this particular case, all measurements are taken from the *cis*-side, i.e., from the same side of the specular reflection as the incident illumination.

In the case of the second example, observation is at a constant  $45^\circ$ , and the angle of illumination is initially  $120^\circ$ . The associated angle of specular reflection will then be  $60^\circ$ , which yields a difference of  $15^\circ$  in the angles of specular reflection and observation. However, in this case, observation will be from the *trans*-side, i.e., from the opposite side of the specular reflection, referred to the incident illumination. Subsequent geometries cover angles of illumination of  $110^\circ$ ,  $90^\circ$ ,  $60^\circ$  and  $25^\circ$ . At angles of illumination of  $60^\circ$  and  $25^\circ$  the angles of specular reflection will be  $120^\circ$  and  $155^\circ$ , respectively. In both of those cases, the angles of observation will be on the *cis*-side as shown in Table 1.

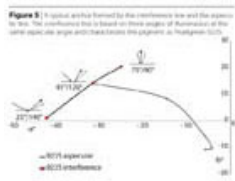
However, measurements on interference pigments clearly indicate that the results of measurements made from the *cis*-side and the *trans*-side will differ, which is why distinguishing between them is essential. Although the absolute values of the aspecular angles involved may be identical, the respective, associated angles of illumination and observation indicate that no comparisons can be made for any, given, angular relationship. If, for example, the angle of illumination is  $45^\circ$  and the angle of observation is  $110^\circ$ , the aspecular angle will be  $25^\circ$ . Although an angle of illumination of  $110^\circ$  and an angle of observation of  $45^\circ$  would yield the same aspecular angle, observation would be from the *trans*-side, and, since the colors exhibited by interference pigments vary with the angle at which they are illuminated, no comparisons of measurements made at  $110^\circ$  and  $45^\circ$  are possible for the same aspecular angle. (Figure 4)



## Choosing the Geometries

The geometries needed for evaluating and observing interference pigments may be derived from their interference properties. Paints containing interference pigments are usually treated in the same manner as metallic paints. Measurements are made at specified angular intervals, referred to the angle of specular reflection, which yields a series of measured spectral data.

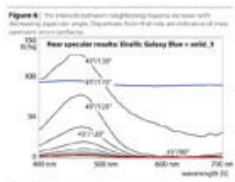
Analyses of data acquired for three or four aspect angles are frequently regarded as sufficient, although they cover, and employ, merely a fraction of the colorimetric data available. Since the color shift toward shorter wavelengths is a property peculiar to the interference pigment involved, it should be employed in visually and instrumentally characterizing interference pigments.



Starting at a steep, near-normal angle of illumination, the angle of illumination is varied through the traditional 45° to the case of flat, near-grazing incidence. It is sensible and practicable to employ a flat angle of illumination of 25°, for which illumination presents no particular problems. Employing flatter angles of illumination might lead to erroneous results.

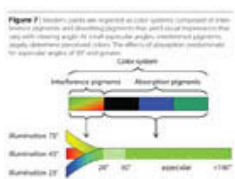
In the case of steeper angles of illumination, illumination at 70° or 75° has been found to be the best choice, since, firstly, the differences between measurement results obtained for the two choices will be slight, and, secondly, employing a steeper angle of illumination might be impossible due to limitations imposed by the setup employed.

For an angle of illumination of 75° and an aspect angle of 15°, measurements will be made at 90°. However, the light source and detector head might interfere with one another for smaller aspect angles. Furthermore, at an angle of illumination of 75°, the observation angle will be identical to that for an angle of illumination of 45°, since the aspect angle, 45°, will be identical to the 15° aspect angle employed in the case of a 75° angle of illumination.



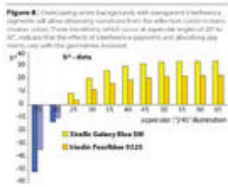
Hypothetically, although making a statement for just two, different angles of illumination (a steep angle at near-normal and flat angle at near-grazing incidence) would be feasible, employing a third angle of illumination would predict the shape of the interference line, which might well extend over three quadrants of the  $a^*b^*$ -coordinate system in the case of pigments that exhibit colors that are strongly dependent upon angle of illumination. (Figure 5)

When considering suitable choices of metrological geometries, there arises the question of how close to the angle of specular reflection measurements can, and should, be made. Based on my personal experience, it may be stated that a minimum displacement of 15° will be sufficient, as well as present no problems due to artifacts. Measurements made at aspect angles less than 10° frequently exhibit irregularities and disagreements, particularly in the case of samples overcoated with clear lacquers. According to the laws of physics, the intervals between maxima will increase as the angle of observation approaches the angle of specular reflection. If the intervals between maxima for aspect angles of 10° and 15° should be less than those for aspect angles of 15° and 20°, the decreases observed will most likely be artifacts. (Figure 6)

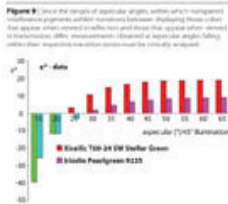


Another reason for making measurements for an aspect angle of 15° is that interference pigments exhibit their full range of interference colors at angles of observation close to the angle of specular reflection. Observing and making measurements at angles farther to the angle of specular reflection will cause shifts to the transmission color. The green of pigments, such as Skarabaeus Red, displayed when viewed at the angle of specular reflection, will change to orange-brown when viewed at displacements of 20° from the angle of specular reflection.

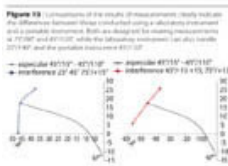
If transparent interference pigments (Iriodin or Xirallic), or similarly formulated paints, are applied to a white background, the proportion of interference pigment involved may be determined from the overall impression of the color it yields. (Figure 7) The color that it exhibits when viewed in and near reflected light will change to the respective complementary transmission color when the aspect angle is 25° or 30°. For example, at an aspect angle of 15°, the blue color reflected by the outer surface of the pigment will be observed.



At larger aspecular angles, the yellow transmission color reflected by the white background will be observed. From that behavior, it may be concluded that interference pigments contained in paint admixtures determine the overall impressions of the latter at aspecular angles under 25°. At aspecular angles greater than 25° or 30°, the overall impressions they create are largely determined by the absorbing pigments contained therein. (Figures 8-9)



In summary, it may be concluded that three, different angles of illumination are necessary, and that measurements close to the angle of specular reflection, at an aspecular angle of 15°, should be conducted for each of them. Additional measurements for a constant 45° angle of illumination and various aspecular angles will be necessary in order to acquire overall color impressions. Aspecular angles of 25°, 45°, 75° and 110°, referred to the angle of specular reflection, 135°, are commonly employed. However, it should be noted that the last aspecular angle mentioned, 110°, will frequently yield measurements that are seemingly in disagreement with one another, which is why that particular aspecular angle should not be employed. The detector signals involved will also be extremely weak.



Furthermore, most users will presume that visual observations, where viewing takes place at that particular aspecular angle, while holding the panel in front of a window, are desired. If one were to accurately reproduce the angular relationships involved there, they would be observing from a vantage point situated in their own shadow, since they would have to be standing with their back to the window. There is thus need for further investigation of results that would be obtained in this manner.

Measurements made at various angles of illumination for the same aspecular angle yield an interference line that is peculiar to the particular interference pigment involved. Measurements made at a constant angle of illumination, e.g., 45°, for various angles of observation and aspecular angles yield an aspecular line. Together, those two lines resemble an anchor, where neither is necessarily a straight line. Particularly “traveler” pigments, which exhibit much more extensive color changes than so-called “shifter” pigments, may exhibit highly complex interference lines. Although aspecular lines usually all have a uniform shape, they might well extend over several quadrants of the a\*b\*-coordinate system in the case of diffraction pigments.

Table 2 The geometries that should be observed in laboratory settings for a range of illumination angles. The table illustrates pigments may be easily characterized by measuring results for three different angles of illumination.

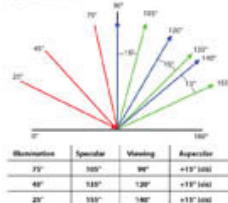
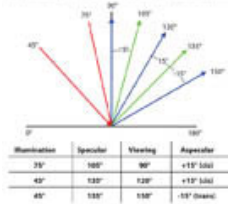
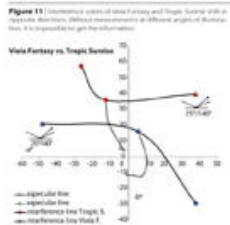


Table 3 Observation of the angles that are observed in the case of pigments, in which color measurements are obtained at the negative of the specular angle at 45° illumination are employed in the first data point.



## Employment of the Geometries Involved

Several of the numerous, feasible, metrological setups have been found to be at least essential for measuring interference pigments and paints pigmented with them. (Tables 2, 3) As mentioned above, the interference lines of the pigments involved reflect their optical properties. Their interference lines are often curved, which is why at least three data points obtained for differing angles of illumination will be necessary for defining them. (Figure 10) Since another three or four data points will be needed for defining their aspecular lines, the optical properties of interference pigments may be adequately described using measurements obtained for a total of five or six geometries, where it should not be forgotten that the choice of the angles to be involved, e.g., illumination at 45°, is both arbitrary and dependent upon the designs of the instrumentation to be employed. The matter of whether the results obtained agree with visual assessments conducted in front of windows or in light booths is initially ignored.



## Discussion of the Application Areas Involved

Multi-angle spectrophotometers that employ either a fixed angle of illumination and several angles of observation, or *vice versa*, are currently employed for measuring the properties of interference pigments. Data obtained for at most three, and sometimes just two, of the various, feasible, geometries is taken into account in the subsequent analyses. The application areas range from the automotive and manufacturing industries, through the paint-manufacturing industry, to the pigment-manufacturing industry. Additional geometries are employed in all industries that utilize either interference pigments or paints pigmented with them.

In general, interference measurements allow determining the optical properties of interference pigments. They also yield key representations of the courses of color curves in the  $a^*b^*$ -coordinate system. Distinguishing between two pigments, such as Viola Fantasy, whose color varies from red-violet, through yellow, to green and Tropic Sunrise, whose color varies over the same spectral range, but in the reverse order, would be impossible without such measurements. (Figure 11) In the case of refinishing operations and OEMs, unknown paint formulations may be determined much faster, more simply, and more reliably utilizing the results of interference measurements. Every interference pigment has a unique “fingerprint” ascribable to measurements conducted for various angles of illumination at a constant aspecular angle.

Since overall impressions of the colors exhibited by interference pigments consist of several components, admixture formulations may be devised more rapidly, and thus at lower cost. In many cases, the total numbers of paint admixtures required and constituents of paint formulations may be reduced if both the interference and absorption contributions are measured employing this “holistic” method.

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