干涉颜料的光学性能——其描述和表征的方法

Optical Properties of Interference Pigments — Solutions to the Problem of their Description & Characterisation

美国材料标准E2539"多角度干涉颜料颜色测量标准"，列举了干涉颜料测量方法的几何参数（**表1**）。这些方法的收集基于大量的仪器和视觉评估技术，其目的在于将物理需求与技术可执行方案结合起来。一方面，我们需要这类颜料的光学性能结果；另一方面，我们具备大量技术可行性，和实现这些技术所采用的可携式计量仪器。

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一般来说，对于如何解决干涉颜料的着色分析问题必须通过两个渠道进行，其解决方案未使用任何计量仪器进行测量，这导致无法对所得的结果进行讨论。相反，更重要的是解决方案应着重关注干涉颜料的光学性能，并将其与所涉及到的计量仪器相关联。由于镜面反射是它的一种光学性能，测试产生的角度也会在视觉评估中起到关键作用。这种条件通常被忽略，因此使用者对于视觉评估结果和仪器测量结果的差别常感到惊讶。

应用于汽车或者其它仪器设备的颜料按照其对入射光的回应分为三种类别。着色涂料部分吸收入射光并将吸收的入射光大量的转化成热量。剩余部分被分散到各个方向，也就是说，所有未被吸收的波长将被广泛分散。荧光或磷光涂料代表了一种特殊情况，它们可以立即或经过一段时间后将紫外光转化成可见光。如果入射光被颜料反射，那意味着

ASTM Standard Practice E2539, entitled "Standard Practice for Multiangle Colour Measurement of Interference Pigments", lists the recommended geometries for measuring interference pigments (**Table 1**). The basis for that collection of geometries is numerous instrumental and visual-assessment techniques aimed at combining the physical requirements with technically feasible implementations. On the one hand, we thus have the necessary conditions that result from the optical properties of such pigments; on the other, we have the feasibility of the various techniques and their implementation in the form of portable metrological instrumentation.

In general, deliberations regarding how the problem of conducting colourimetric analyses of interference pigments might be solved must be approached via two avenues, and its solution does not involve employing just any metrological instrument, making measurements with it, and then failing to

表1：依照美国材料标准E2539测量干涉颜料的几何条件
Table 1: The geometries to be employed in measuring interference pigments in accordance with ASTM Standard Practice E2539

光照 Illumination*	观测 Observation*	反射 Aspecular	ASTM
15°	0°	15°	15°: 0° (as 15°)
15°	-30°	-15°	15°: -30° (as 15°)
45°	-30°	15°	45°: -30° (as 15°)
45°	-60°	-15°	45°: -60° (as -15°)

*偏离正常的角度 Angle relative to the normal

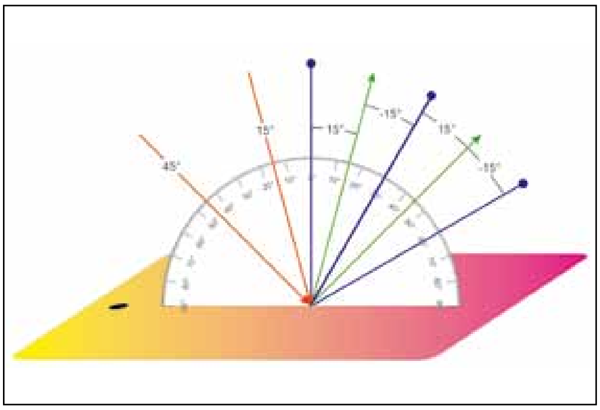

图1：恒定45°光照的传统几何条件的说明
Figure 1: An illustration of traditional geometries involving a constant 45° angle of illumination

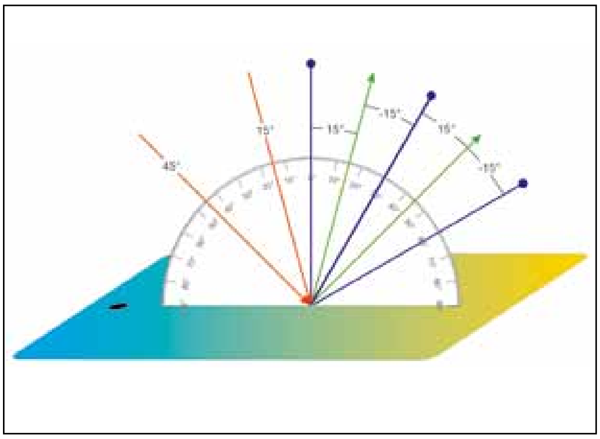

图2：镜面反射下，偏轴角位移为±15°下的测量结果组合
Figure 2: A combination of both types of illumination involving measurements taken at angular displacements of +/- 15° from axes, along which specular reflection occurs

存在反射颜料颗粒，这种颗粒通常是铝箔。反射光会或多或少地变强并伴随光闪，其程度取决于颗粒的大小。

不同于这两种颜料，干涉涂料将入射光分成反射光线和折射光线，引起选择性波长的反射（**图1~2**）。其结构由高折射率的单层或多层结构组成，这导致在分层结构表面发生反射，并在结构内部发生折射。传统的干涉涂料采用天然云母薄片作为基材，其上涂覆一层很薄的高折射率金属氧化物薄膜。常用的金属氧化物是二氧化钛、氧化铁、氧化铬或者是其中的两种或两种以上金属氧化物的混合物。

云母基材颜料上的入射光将会在其外表面发生部分镜面反射。其余的光将通过二氧化钛等高折射

conduct any discussions of the results obtained. On the contrary, more important is taking a close look at the optical properties of interference pigments and correlating them to the capabilities of the metrological instrumentation involved. Since specular reflection is one of their optical properties, the angles at which measurements are made will also play a key role in visual assessments, and not just in determining the instrumental techniques employed. That requirement is usually forgotten, and users wonder at the differences between the results obtained from visual assessments and instrumental measurements.

Classifications of the pigments employed in automotive and other industrial applications yield three major groups that differ in their responses to incident light. Coloured pigments partially absorb incident light and largely transform the absorbed portion into heat. The remainder will be scattered in all directions, i.e., all wavelengths that have not been absorbed will be diffusely scattered. Fluorescent or phosphorescent pigments, which either instantly, or over extended periods, transform UV-light into visible light, represent a special case. If incident light is specularly reflected by pigments, then the reflective pigment particles, which will usually be aluminum flakes, are present. The reflected light will be more or less intense and sparkling, depending upon their dimensions.

Unlike those two types of pigments, interference pigments split incident light into reflected and refracted beams, causing wavelength-selective reflections **(Figures 1~2)**. Their composite structures consisting of one or more layers having high indices of refraction lead to reflections at, and refractions within, their layered structures. Traditional interference pigments contain natural-mica platelets that serve as substrates for high-index metal oxides applied to them in the form of very thin films. The metal oxides commonly employed are titanium dioxide, iron oxide, chromium oxide, or combinations of two or more such metal oxides.

Light incident on mica-based pigments will be partially specularly reflected at their outer surfaces. The remainder will be refracted upon entering the higher-index medium, e.g., titanium dioxide. Light will be partially reflected again at the interface between the titanium dioxide and the mica platelets and exit the pigment parallel to the first partial reflection. The two partially reflected beams are thus confined to interacting with one another only, causing the effect termed "interference." Due to the different lengths

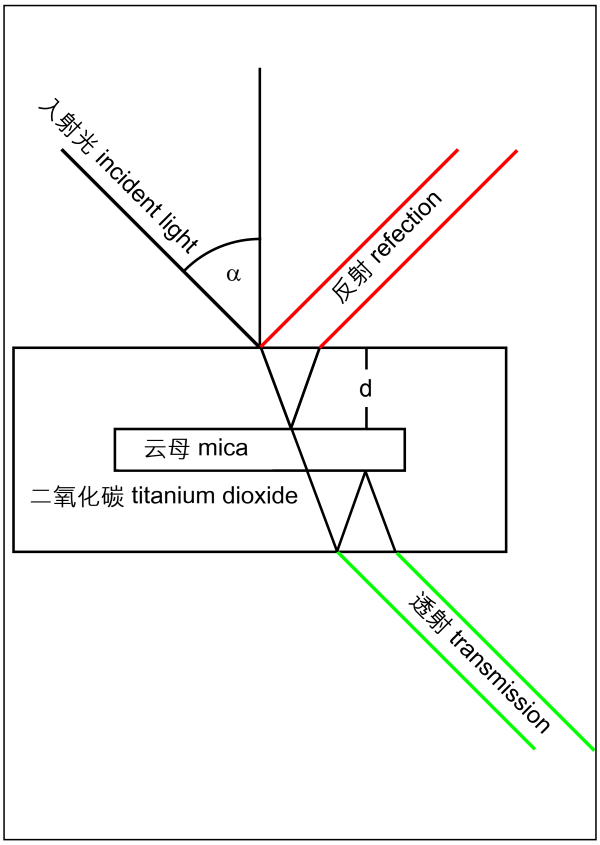

图3：入射α光线的角度和二氧化钛薄膜厚度对反射光的表面着色影响较大，透射光将补充着色

Figure 3: Angles of incidence α and titanium-dioxide film thicknesses d strongly affect apparent colourations in reflected light. The transmitted light will have complementary colourations

率媒介被折射。部分光又在二氧化钛和云母薄片的内表面间进行多次反射，最后离开颜料平行面汇入初始反射部分。假定这两部分反射光线只发生彼此的相互作用，这就引起"干涉"效果。由于在给定时间内穿过路径的长短不同，在从低折射率到高折射率媒介转化过程中，两个光线的相位会相互转变。如果一个波的波峰与另一个波的波峰重合，就会发生正干涉。如果一个波的波峰与另一个波的波谷重合，就会发生负干涉。

波长被放大的程度主要取决于金属氧化薄膜的厚度和入射光的入射角度（**图3**）。膜层的厚度由制造过程决定并与各种干涉颜料自身的特性有关。使用更厚的二氧化钛膜层会使反射波峰向长波长转化，导致反射光着色的颜色从白色逐渐变成黄色、红色、蓝色，最后变成绿色（**图4**）。颜色的不规则分布是由于零级反射波峰（白色）和最小反射率的作用，而另一个反射波峰落至可见光谱区域之外。在向长波长转化的情况下，即涂层增厚引起转化，

of the paths traversed during given time periods and the phase shifts occurring at the transitions from lower-index to higher-index media, the phases of the two beams will be shifted relative to one another. If a wave crest coincides with a wave crest, constructive interference will occur; if a wave crest coincides with a wave trough, destructive interference will occur.

Which wavelengths will be amplified will primarily depend upon the thicknesses of the metal-oxide films and the angle of incidence of the incident light **(Figure 3)**. Their film thicknesses will be determined by the manufacturing processes employed and yield the typical, basic colourations of the respective interference pigments involved. Employing greater titanium-dioxide film thicknesses will shift reflectance peaks toward longer wavelengths, yielding shifts in colourations in reflected light ranging from white, through yellow, red, and blue, to green **(Figure 4)**. That unusual ordering of colourations is due to the fact that the zero-order reflectance peak (white) is followed by a reflectance minimum and another reflectance peak falling outside the visible spectral region. In the case of the shift toward longer wavelengths, i.e., the shift caused by employing greater film thicknesses, the reflectance minimum will be shifted into the visible spectral region, yielding a yellowish colouration in reflected light. Further such shifting toward longer wavelengths will yield red, and, subsequently, blue, colourations, since that will shift the second reflectance peak into the visible spectral region and

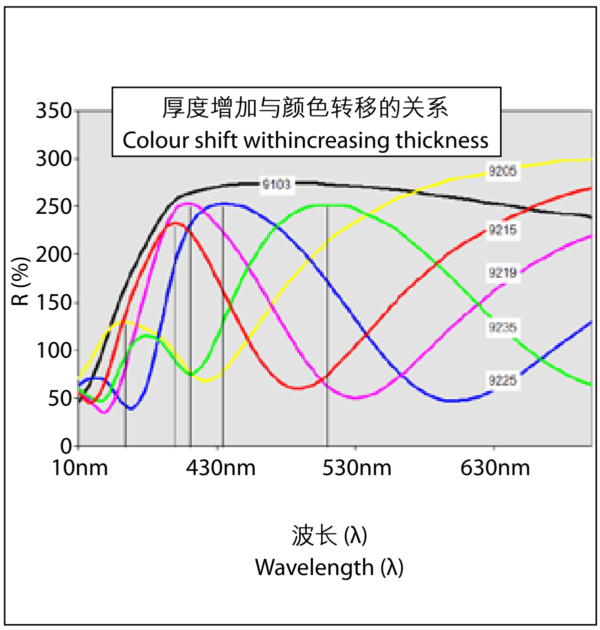

图4：二氧化钛薄膜厚度的增加使反射峰向长波长方向移动

Figure 4: Increasing titanium-dioxide film thickness shifts the reflectance peak toward longer wavelengths

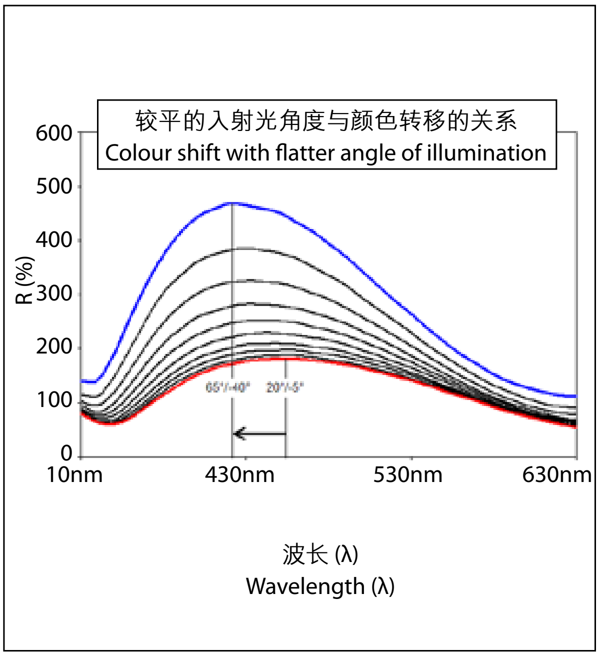

图5：入射光角度增大使反射峰向短波长方向移动
Figure 5: Increasing the angle of incidence shifts the reflectance peak toward shorter wavelengths

最小反射率将会被移至可见光区域，从而在反射光着色时产生淡黄色。进一步向长波长转变会产生红色、蓝色，因此可将第二个的反射波峰转化至可见光区域，并将第一个反射波峰转化至红外光谱区域。进一步增厚涂层将会使反射波峰从蓝光转化成绿光区域。

由于膜层厚度和由此决定的反射光着色效果是由加工过程决定的，不能改变。因此，它们不能作为干涉颜料颜色分析的手段。影响颜色的另一重要因素是光照角度。改变入射光的角度将可以观察到典型的干涉效果。随着入射角的增加，颜色将会相短波长转变（**图5**）。相反地，减小入射角度，颜色将会朝长波长转变。这些典型特点可以用来表征和鉴别干涉涂料。

当光线经其通道通过干涉涂料时，相似的反射和折射现象将持续发生直到光线从颜料远端消失。由于逐渐减少的相位转变只发生在低折射率和高折射率介质介面之间，因此透射光的颜色将会补充反射光颜色。

简言之，包含不同折射指数的多层结构涂层，各涂层的折射率差别巨大。它们的颜色是由于反射光线和折射光线的相互作用。不同于着色颜料，由于不同的处理过程，其着色通常会随着时间变化，而干涉产生的颜色会保持数百万年不变，例如可以

shift the first reflectance peak into the infrared spectral region. Further increases in film thickness will then shift the reflectance peak from the blue to the green spectral region.

Since film thicknesses, and therefore the resultant colourations in reflected light, are determined by manufacturing processes and cannot be changed, they cannot be employed as a means for conducting colourimetric analyses of the interferences involved. Another factor that has a major impact on colouration is the angle of illumination. Changing the angle of incidence will allow observing typical interference effects. The resultant colouration will be shifted toward shorter wavelengths when the angle of incidence is increased **(Figure 5)**. Conversely, decreasing the angle of incidence will shift colouration toward longer wavelengths. These typical responses may be employed for characterising and identifying interference pigments.

As light progresses along its path through interference pigments, similar reflections and refractions will continue to occur until the light exits from pigments' far sides. The resultant colouration in transmitted light will be complementary to that in reflected light due to the lack of the phase shifts that occur exclusively at interfaces between lower-index and higher-index media.

In short, multi-layered structures consisting of layers having differing indices of refraction exhibit spectrally selective reflectances. Their colourations are due to interactions between reflected and refracted beams. Unlike colouring pigments, whose colourations usually change with time due to various processes, colourations due to interferences may persist for millions of years, as may be observed in the case of the colourations of, e.g. fossil, primeval beetles, and their optical properties may be determined by changing the angle of incidence of incident light.

We therefore have, on the one hand, the optical properties of interference pigments, and, on the other, the design specifications of colourimetric instrumentation, which usually specify fixed illumination and observation geometries. Furthermore, in the case of, e.g. portable instrumentation, their engineering specifications effectively eliminate illumination at grazing incidence. Implementing such large angles of illumination would make them much larger, which would be undesirable.

Portable instrumentation featuring collimated illumination at 45°-incidence has been introduced

表2：恒定45°光照的传统几何条件也被用于观测干涉颜料
Table 2: Traditional geometries involving a constant 45° angle of illumination are also employed for measuring interference pigments

光照 Illumination*	观测 Observation*	反射 Aspecular	ASTM
45°	-30°	15°	15°: -30° (as 15°)
45°	-20°	25°	45°: -20° (as 25°)
45°	0°	45°	45°: 0° (as 45°)
45°	30°	75°	45°: 75° (as 75°)
45°	65°	110°	45°:1100° (as 110°)

*偏离正常的角度 Angle relative to the normal

观察到的化石、原始甲虫等的颜色，而且它们的光学性能可以由入射角角度的改变而决定。

因此，我们一方面掌握了干涉涂料的光学性能，另一方面，掌握了颜色测试设备的设计规格，该规格指定了固定的光照和观测方法。不仅如此，便携设备的设计标准有效消除了临界入射光照。如果实施很大的光照角度则会使得设备的体积增大，将增加设计的难度。

以45°平行光入射为主要特点的可携式仪器已经被应用于测量铝颜料的着色效果（**表2**）。这类仪器测量反射角度为15°、25°、45°、75°和110°的光强度。这种方法不适于测量干涉，而只能适合于测量某种特定情况下的干涉，这一点易被实验证明。如果透明干涉颜料被应用于白色基材上，其从反射光颜色到透射光颜色的转变将发生在自轴线起角位移为20°到30°处，并随着镜面反射（**图6**）。如前所述，透射光的颜色是反射光折射的补充。发生镜面反射时，接近于轴线下的视觉和仪器测量将使颜色归因于反射光。然而，在偏离轴线下观察透明颜料将可非常详尽地观测，而且可以看到在白色底面上，透射光的补充颜色被反射出来（**图7**）。

测量干涉颜料的必备条件是至少需要采用第二或者第三光照角度，测量干涉颜料产生的干涉效果也是如此。但是，对于可携式仪器来说，采用第三光照角度可能在技术角度不可行，因此美国材料标准E2539对此未详尽说明。

具备两个光照强度的新型设备可以带来什么便利因素？答案是不再需要大量的用于描述和表征干涉颜料的技巧。与此相反，它们提供一种涉及深层几何尺寸的方案，这种方案也已经被美国材料标准E2439重新加以解说。除在偏离镜面反射15°角度下观测值之外，-15°的观测值也被确定。这些观察和测量发生在光源一侧，而正对于镜面反射处。在15°或45°光照条件下，随着镜面反射的产生，观测

in order to allow measuring effect-colourations of aluminum pigments (**Table 2**). Such instrumentation measures the intensities of light reflected at angles of 15°, 25°, 45°, 75°, and 110° relative to the respective angles of specular reflection. That such geometries are unsuitable for measuring interferences, and only marginally suitable for measuring them only under certain circumstances, may readily be experimentally demonstrated. If transparent interference pigments are applied to a white surface, the transition from their colouration in reflected light to that in transmitted light will occur at angular displacements of 20° to 30° from the axis, along which specular reflection occurs (**Figure 6**). As mentioned above, their colourations in transmitted light are complementary to

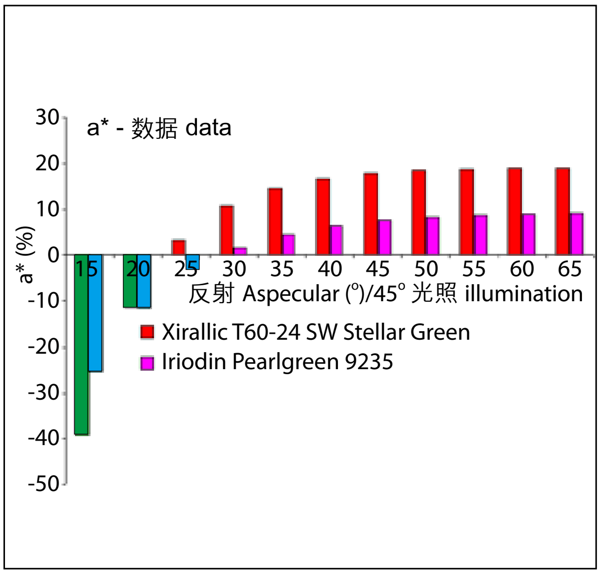

图6：测量白色背景下的反射率，可以观测到当观察角度和镜面反射的角度增大时，从反射光着色到透射光着色的转变
Figure 6: Measuring reflectance against a white background will allow observing the shift from the colouration observed in reflected light to that observed in transmitted light that occurs when the difference between the angle of observation and the angle at which specular reflection occurs is increased

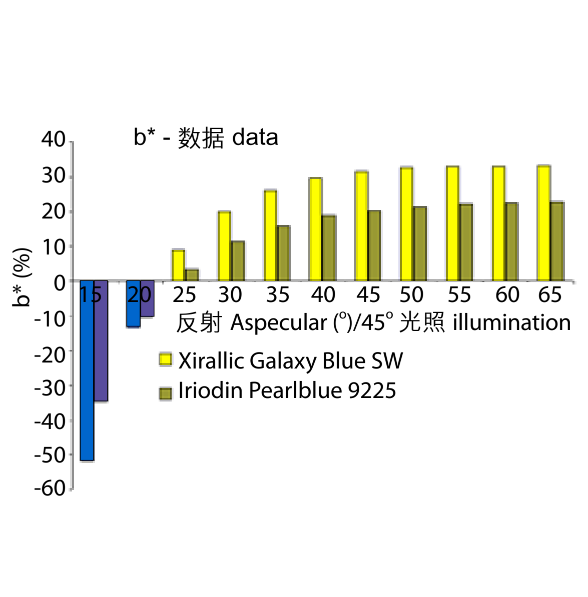

图7：随着镜面反射的发生，随观察角度和镜面反射角度之间差异的变化，通过颜色指数可以检测到反射光着色变成透射光着色的突变。着色变化发生在偏离轴线的角位移20°至30°区域

Figure 7: Plotting colour indices against the difference between the angle of observation and the angle at which specular reflection occurs allows detecting the abrupt shift from the colouration observed in reflected light to that observed in transmitted light. The transition zone occurs at an angular displacement of 20° to 30° from the axis, along which specular reflection occurs

的角度应为偏离轴线角位移的±15°处。

干涉颜料由涂覆相对较薄金属氧化物薄膜的大云母薄片组成。如果被应用于汽车涂料等配方中，其薄片的排列将与应用的基材表面平行。由于其平面的法线与涂层表面相垂直，偏离理论反射角度的角位移+15°的观测值与偏离涂层表面法线15°的观测值相同。因此，反射角等于入射角的法则得到支持，并且这些薄片的光照角度是30°。

与镜面反射理论角度相对，相对角位移为-15°下的观测值是由偏离表面法线60°的光照射薄片而测得。然而，所得结果并非与+15°角位移下所得结果完全一致，这是由于在计算镜面反射的理论角度时，散射等其它因素也被考虑其中。将偏离理论镜面反射角度角位移分别为+15°和-15°所得反射率曲线进行比较，结果表明短波长向长波长转移的现象的确出现，这与上述说明一致，也验证了上述结论的正确性。

为了更好地描述所发生的干涉现象，假设新的理想条件：15°小角度光照、45°常规光照和相对于薄片表面65°倾斜光照。观察和测量角度都为偏离

those in reflected light. Visual and instrumental observations conducted close to the axes, along which specular reflection occurs, will yield their colourations in reflected light. However, observations of transparent pigments conducted at larger off-axis angles will allow looking through them and seeing the underlying, white surface, where their complementary colourations in transmitted light will be reflected **(Figure 7)**.

Employing at least a second, and, ideally, a third, angle of illumination will be necessary for measuring interference pigments, and thus for measuring the interference effects that they produce. However, employing a third angle of illumination might not be feasible from the engineering standpoint in the case of portable instrumentation, and has thus been left unspecified under ASTM E2539.

What opportunities does new instrumentation featuring two angles of illumination have to offer? The answer is that there will no longer be any need for delving into a bag of tricks in order to solve the problems involved in describing and characterising interference pigments. On the contrary, they offer a solution involving employment of further geometries that have also been redefined under ASTM Standard Practice E2439. In addition to observations and measurements at +15° from angles of specular reflection, further displaced by -15° relative thereto, i.e., conducted on the trans-side, have been defined. Such observations and measurements will be on that side of the illumination source opposite that where specular reflection occurs. In the case of illumination at 15° or 45°, observations and measurements are to be conducted at angular displacements of ±15° from the axes, along which specular reflection occurs.

Interference pigments consist of large mica platelets having relatively thin metal-oxide coatings. If they are employed in formulating, e.g. automotive paints, their platelets will endeavour to align themselves with their planes parallel to the surfaces to which they are applied. Since the normals to their planar surfaces will be normal to painted surfaces, observations and measurements conducted at angular displacements of +15° from theoretical angles of specular reflection will be of those pigment platelets whose normals to their surfaces are tilted through 15° relative to the normals to painted surfaces. The law stating that the angle of reflection equals the angle of incidence will then be upheld and the angle of illumination for such platelets will be 30°.

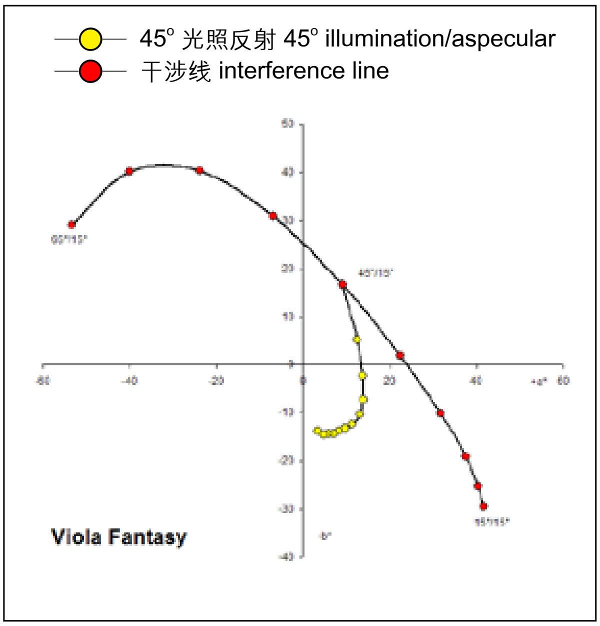

图8：干涉曲线和反射角-反射率曲线的叠加可以做到具体描述干涉颜料的光学性能
Figure 8: Superimposing their interference lines and aspecular-reflection lines allows arriving at accurate descriptions of the optical properties of interference pigments

镜面反射理论角度15°。研究表明，65°光照不符合几何规则，并在所有情况下，偏离镜面反射理论角度15°位移下所得观察结果和测量值均可由45°光照的反式-几何规则代替，并可由-15°观测值代替，以下缩写成45°/代替-15°。

因此三个几何规则45°/代替-15°，45°/代替+15°，和15°/代替+15°代表了一个恰当的组合，也可合理替代三个不同光照角度。所有测量和计算干涉现象的资料都服从该理论，这意味着这种结论是具有概括性的（**图8**）。

当采用与其镜面反射角度远远不同的角度进行观测时，对于干涉颜料或者含有这种颜料的涂料进行更深层描述时，也必须包含其明显的光学性能。在工业应用中，干涉颜料通常与着色颜料或者含铝颜料混合使用。由于大多数干涉颜料都或多或少的透明，生产的遮盖涂料可以采用适合于大批量喷漆操作的着色颜料混合使用。包覆二氧化钛的干涉颜料通常与黑色、蓝色或绿色颜料混合，将其与黄色或红色等明亮颜料混合，可以得到低亮度的颜料。

除干涉效果之外，光学特性的作用还在于研究折射率和反射率。后者可以采用传统计量几何进行描述，该描述使用单一光照，涉及不同的观察测量

On the opposite side of the theoretical angle of specular reflection, observations and measurements conducted at angular displacements of -15° relative thereto will involve illuminating such platelets at 60° to the normals to their surfaces. However, the results obtained will not be exactly identical to those obtained at +15°, since other properties, such as scattering etc., are taken into account in computing theoretical angles of specular reflection. Comparing the reflectance curves obtained at angular displacements of +15° and -15° relative to the theoretical angles at which specular reflectance occurs shows that shifts from shorter to longer wavelengths corresponding to those mentioned above actually occur, which confirms the statements made above.

Assuming, once again, ideal conditions, in order to optimally describe the interferences that occur, a small angle of illumination of 15°, illumination at the traditional 45°, and oblique illumination at 65° to the normals to platelets surfaces would be needed for the respective, equal angles of observation/measurement of 15° relative to the theoretical angles at which specular reflection occurs. Studies have shown that the unimplemented geometry involving illumination at 65° and observation/measurement at a 15° displacement from the theoretical angles at which specular reflection occurs may, in all cases, be replaced by the trans-geometry involving illumination at 45° and observations/measurements of aspecular (as) reflectances at -15°, which will hereinafter be abbreviated to 45°/as -15°.

The three geometries, 45°/as -15°, 45°/as +15°, and 15°/+15°, therefore represent a reasonable combination and an acceptable alternative to a combination involving three, differing angles of illumination. All measurements and computations of interferences that have been conducted to date have yielded the same conclusions, which means that those conclusions may be generalised **(Figure 8)**.

The further description of interference pigments, or paints containing such pigments, also entails describing those of their optical properties that become apparent when they are viewed at angles far from angles at which specular reflection occurs. In industrial use, interference pigments are usually mixed with colouring pigments and/or aluminum pigments. Since most interference pigments are more or less transparent, covering paints involving their admixture with colouring pigments that are suit-

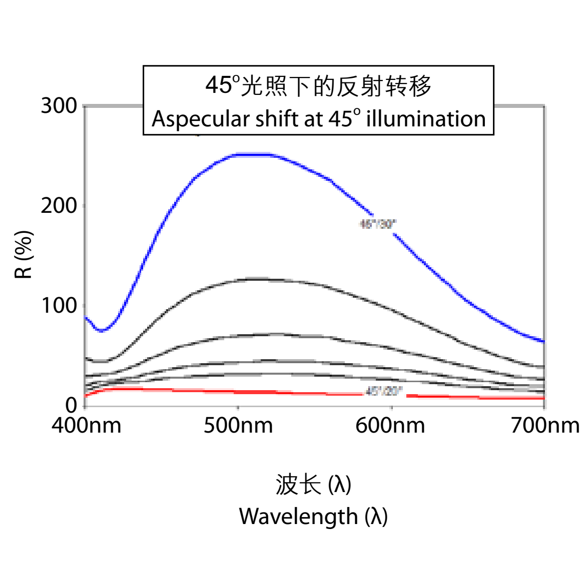

图9：计量几何条件的不同效果。几何条件接近反射角-反射率的坐标轴效果最大
Figure 9: The effects of metrological geometries are of varying magnitudes. Geometries that involve making measurements close to specular-reflection axes have the largest effects

角度以及不同的镜面反射发生的角度（**图9**）。具体地说，光照角度为45°，测量角位移分别为偏离镜面反射轴线15°、25°、45°、75°和110°。然而，由于经常涉及出现伪影，需要对后面的角度替代条件下测试的结果进行仔细检查。

结语

美国材料标准E2539列出了描述干涉颜料光学性能的几何条件。选择并组合使用几何条件，可以表征任何干涉颜料的典型特征。一方面，干涉线描述了增加一个光照角度导致的干涉现象。在原有45°光照条件下，增加一个15°光照。观察和测量角度为偏离轴线15°角位移，随着每一个光照角度都发生镜面反射。在45°光照条件下，也需要进一步测量-15°光照的结果。综合三个角度的测量结果，可以得到一条干涉曲线。

另一方面，综合45°光照下±15°的测量结果可以得到一条反射角-反射率曲线，该曲线明确表明了吸收和散射的作用效果。

两条曲线都表明了干涉颜料的主要光学性能，并可以使其应用于所需领域。由颜料批次导致的差异和干涉颜料在颜料样品图形的特征都可以忽略。

able for use in mass production painting operations may be manufactured. Interference pigments having titanium-dioxide coatings are usually combined with black, blue, or green colouring pigments. Combining them with bright colouring pigments, such as yellow or red pigments, yields less attractive paints.

In addition to interference effects, their optical properties of interest also include their absorptivities and reflectances. The latter may be described by employing traditional metrological geometries involving a single angle of illumination and various choices of differences between the angles at which observations/measurements are conducted and the angles at which specular reflection occurs **(Figure 9)**. In concrete terms, that implies a 45° angle of illumination and measurements conducted at angular displacements of 15°, 25°, 45°, 75°, and 110° from specular-reflection axes. However, the results of measurements conducted at the latter angular displacement should be critically viewed, since recurrent artifacts will usually be involved.

Summary

ASTM Standard Practice E2539 lists the geometries that should be employed in arriving at descriptions of the optical properties of interference pigments. Careful choices of geometries and combinations thereof will allow characterising the typical properties of any interference pigment. On the one hand, interference lines describe the interference phenomena resulting from adding a second angle of illumination, 15°, to the traditional 45°. Observation/measurement will be at an angular displacement of 15° from the axis, along which specular reflection occurs for either angle of illumination. In the case of illumination at 45°, further measurements at -15° are also to be included. The results of measurements at all three angles are then combined, yielding an interference line.

On the other hand, combining the results of measurements at ±15° for 45° illumination will yield an aspecular-reflectance line, which is largely an indication of contributions due to absorption and scattering.

Both lines represent indications of the major optical properties of interference pigments and may be utilised for tailoring them to suit their intended applications, regardless of whether it be determining differences between batches of pigments or paints, or for the characterisation of interference pigments on paint-sample charts.