A Method to Evaluate the Near and Far Aspecular Reflectance Differences of Organic Pigments and Possible Causes

A review and examination of color travel of organic pigments in thermoplastic materials is undertaken. A method of how to quantify and understand the color changes and how to predict performance based on particle morphology is put forward.

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Abstract:

Technical personnel working in the color industry are familiar with the shading concepts exhibited by various organic pigments. Reds are described as yellow shade or blue shade, blues are similarly described as being green or red shade, and yellows are described similarly. It has recently been commented that there is a degree of color travel that can be observed with organic pigments within a given application. This travel is seen when a single object is viewed from multiple angles. This travel is visually similar to what is observed when evaluating the performance of some effect pigments, particularly those known as interference pigments. This property, correctly referred to as near and/or far aspecular reflectance, may be more commonly known by its generic term “travel”, the difference between flash (facing you) and flop (the down angle away). The first goal of this paper is to further define this phenomenon as it applies to organic pigments and discuss a method by which it can be quantified. It is hypothesized that this behavior may be related to particle size, distribution, or pigment crystal morphology. The second goal is to provide examples of this phenomenon, report on the technique, and use this technique to examine the behavior relative to the above pigment characteristics.

Introduction:

The visual phenomenon when color changes based on viewing angle has been known in the colorant industry for some time. While this is commonly observed when effect pigments are in use, a similar change in color can be observed when using only organic pigments. The development of the multi-angle spectrophotometer (as opposed to fixed angle or spherical diffuse) allows for characterization of this color travel in a numerical fashion. This characterization takes the form of the familiar CIELab* or CIELCH* values and reflects the change in color that is seen visually as the viewed object rotates toward or away from us. This characteristic, near aspecular reflectance or far aspecular reflectance, is probably more commonly known by industry practitioners as travel, flop, or perhaps flash and flop. Flop is defined as when the viewed object "flops" away from the observer, and flash is defined as it is rotated toward the viewer.

For the general purpose of this paper, the terms of travel and flop will be used interchangeably.

As suggested above, this phenomenon is most commonly referred to in relation to effect pigments. However, recent investigations showed a formulated blue shade black that demonstrated a color change. In this instance, the color change was observed to move to a red shade. The injection molded part was mounted vertically and the change in color was seen in a horizontal viewing plane.

By using a multi-angle spectrophotometer that measured reflectance and calculated CIELabCh* at -15, 15, 25, 45, 75, and 110 degrees, it was possible to identify and confirm the color shift that was being observed visually. The formulated black made use of a phthalocyanine pigment to provide the preferred blue undertone. Because the underlying black was a carbon black well dispersed and not known to exhibit color travel, the question of the travel was investigated as though the phthalocyanine component was the source of the travel. Experimentation with a variety of phthalocyanine pigments ultimately developed a formulated blue shade black that demonstrated a reduced tendency to exhibit this color travel. This naturally led to more questions. Why did this blue work when others did not? Can flop be identified in relation to other blue pigments? Can flop be identified in other pigment colors and chemistries?

Hypothesis:

Taking the last question above into consideration, a hypothesis was put forward:

Organic pigments exhibit color travel independent of the presence of effect pigments. (This phenomenon is known in the automotive coatings industry.) It may be possible to instrumentally identify and quantify this behavior using multi-angle spectrophotometric techniques. Further, if this behavior can be identified and quantified, it may also be possible to tie this behavior to some physical parameter characteristic of the pigment, therefore making the phenomenon predictable.

Experimental:

An experiment was performed to evaluate a variety of pigments to identify if and to what extent could color travel be identified. A second goal was identified to determine if there were physical parameters of a pigment that might facilitate a prediction of color travel. To accomplish these

goals a series of pigments of varying chemistries, particle sizes, and shapes were identified. The individual pigment chemistries, and certain physical parameters can be found in Table 1, chemical structures are shown in Appendix 1. In several instances, multiple samples of equivalent chemistries, but different particle size or morphology, were tested.

The next task was to determine a methodology for evaluation. Considering those performed experiments related to identifying the color travel observed in the formulated black, it was decided to take a similar approach to collecting the data in this experiment. In the original experiment, material had been compounded and then injection molded. The color was measured using a Byk-Mac multi-angle spectrophotometer that measured the CIELabCh* at -15, 15, 25, 45, 75, and 110 degrees. This data was recorded and the change in color in the a* parameter was evaluated, as the registered concern was color change from green shade to red shade. This original work was performed in ABS.

It was concluded that, in addition to the multi-angle capability, the test needed to be something that could be easily performed, facilitate quality control work, and would allow for possible alignment of particles. It was decided to perform dispersion in flexible PVC using a two roll mill to accomplish dispersion. Mill sheets were allowed to equilibrate for a minimum of 24 hours at room temperature before reading the color. Color was read directly from the mill sheet machine side. Five readings were taken in both the machine direction and at 90 degrees to the machine direction. These were averaged to represent two values, machine and 90 degrees. The mill sheet was approximately 40 mil thick and always read over the black portion of a Leneta card to provide a uniform background. The LabCh* values were collected and tabulated for each sample. Loading was typically at 0.2% by weight.

Results and Discussion:

In reviewing the data below, it is important to recognize that surface area was reflective of particle size. However, the use of light scattering techniques to determine particle size may be dispersion dependent and not reflective of potential porosity issues. It was decided to employ the surface area parameter as a basis of comparison.

Table 1, Pigment Physical Parameters

Pigment	Chemistry	BET Surface area	Particle Size Light scatter	Particle Shape TEM
PY138 #1	quinophthalone	31.6m2/g	510nm	Amorphous
PY138 #2	quinophthalone	9m2/g	1076nm	Amorphous
PY110 #1	Isoindolinone	26.7m2/g	840nm	Acicular
PY110 #2	Isoindolinone	8.6m2/g	1600nm	Amorphous
PO 71	DPP	81m2/g	1770nm	Acicular
PO73	DPP	20.8m2/g	1110nm	Acicular
PR254 #1	DPP	15m2/g		Amorphous
PR254 #2	DPP	13.5m2/g	570nm	Amorphous
PR254 #3	DPP	25m2/g		Amorphous
PB15:4	PCN	79.5m2/g	2,280nm	Acicular
PB15:6	PCN	73m2/g		
PB15:1	PCN	61.1m2/g	1680nm	Amorphous
PB15:3	PCN	49		Acicular

The color data can be found in the Tables 2 – 4. Examination of the data and the respective plots of the individual parameters versus viewing angles, found in Figures 1 - 12, led to the question of which data has meaning and how should it be interpreted.

The goal of this paper was not to create a new color space definition or technology. The goal was to use an existing tool, the ability to evaluate color in a relatively straight forward manner, i.e. LabCh* and the Delta E parameter. While direct, it was effective, and relatively universal in its application and understanding. Therefore, it made for an excellent tool. The real key was then the ability to evaluate these parameters at a variety of incident light angles. Then, the cumulative data was measured and interpreted in relation to expressing color travel without referring to the impact of effect pigments, which were not present. This led to the question of which parameter was likely to provide the most direct evaluation of color travel.

Experience and convention suggested that the undertone travel of concern varies to some extent with the fundamental color. Yellows were considered to travel from green to red, so were blues.

Reds were considered to move from yellow shade to blue. So, it was determined to examine the a* value in relation to yellows and blues, and the b* value in relation to reds.

Consideration of the DE parameter, Equation 1, from CIELab* was considered first. This parameter does a very effective job in describing the straight-line color difference between two products or perhaps between differing angles. However, it did not seem to differentiate well the difference observed in color change owing to a specific shade change. In this instance, the 1976 version of CIELab* was employed. (While there are more current versions, the available software was limited to this example.)

Eq. 1 $\text{Delta E} = ((dL^*)^2 + (da^*)^2 + (db^*)^2)^{1/2}$

The L* data can be found in Table 2, and the corresponding plots of the data in relation to viewing angle can be found in Figures 1-4. It was decided that this parameter would not provide sufficient differentiation among samples in terms of shifting color undertones. In plotting L* vs viewing angle, the slope was always observed to be negative with increasing viewing angle. Since the L* value is referred to as a "lightness – darkness" parameter and not necessarily indicative of a "chromatic color", this type of performance was viewed as rather a normal circumstance – something to be expected. One point that may be of interest is to observe the curve behavior at about the 45-degree viewing angle. Effectively, all the samples demonstrated an inflection point at this viewing angle. The implication was that the visual change from 45 to 110 degrees may be less significant compared to the first 60 degrees.

The first samples reviewed were the four yellow pigment samples, two PY110 and two PY138. Plotting the a* and b* data from in Tables 3 & 4, Figures 5 and 9, respectively, showed rather different behavior. The first examination was of the a* value, green (negative values) to red (positive values) for the yellows. A simple visual examination of the a* value showed clear differences between the PY 110 and PY138 that was attributable to the chemistry, i.e. the very red PY110 and the very green PY138. Of equal interest was the difference observed in the plots that might be associated with the specific surface areas. The behaviors of the two products were similar in that both demonstrate small movements of the a* value. In the case of the PY110, the shift offered a relatively positive slope (positive a*) moving more red, while the PY138 exhibited a small negative slope (negative a*) moving more green.

At this point, an effort was made to quantify this change in a*. The first approach was to simply look at the net change in the a* value from viewing at -15 degrees to +110 degrees, Equation 2.

Eq.2 $a^*_{(-15)} - a^*_{(110)} = da^*_{(125)}$

The data in Table 3 shows small net changes in the a* value for the smaller surface area products with values of +(5-6) for the PY110 and –(2-3) for the PY138, clearly indicating a red shift for the PY110 and green shift for the PY138. This is compared to a larger red shift for the larger surface area PY110, +(~12), and a larger green shift, -(~3.5), for the larger surface area PY138.

A second approach was to look at the change of a* with respect to how much change per degree, essentially taking an average change of a* per degree of net viewing angle change, Equation 3.

(This should be thought of as an average change as this calculation does not account that in some cases the curves do reverse and assume positive slopes at viewing angles >45 degrees.)

Eq. 3 $da^*_{(125)} / 125 = da^*/dVA$

This resulted typically in a value that was quite small so a simple multiplier was added to make whole numbers instead of fractions, Equation 4. It is this value that is listed in the last column of the tables.

Eq. 4 $10(da^*_{(125)} / 125) = da^*/dVA$

In viewing the value that is provided by Equation 4 in relation to the plots, it is clear that the smaller the da*/dVA value, the flatter the reflectance curve, and the less color travel in the green – red dimension.

Examination of the b* plots in Figure 9 show only positive slopes with only slight points of inflection. Therefore, this indicated that the color is always moving toward a more yellow appearance. There is differentiation in how high on the plot the respective products might place, however, this would generally be expected based on their different colors, and does not appear to be indicative of color travel representing shade changes.

As expected, applying this same method of evaluation to the oranges, PO71 and PO73, shows that the two products are different colors. However, the da*/dVA is similar with only about 0.5 units separating the two products, both having da*/dVA values of 1-2 units. This suggests that there is modest but perhaps not significant travel in the green – red dimension. Applying this method of measurement to the b* value does provide greater separation. Additionally, the db*/dVA offers a larger value of approximately 4-5 units, about twice that of the a* parameter. This points to a higher degree of color travel in the yellow – blue dimension. This suggests that for the orange color space, travel consideration should be thought of in the same fashion as the reds, i.e. yellow shade – blue shade. For both pigments, the larger surface area offers the smaller db*/dVA value supporting the idea that the larger surface area demonstrates less color travel by about 2 units, i.e. the curve is more flat. This is contradictory to the behavior observed in the yellows where the larger surface area demonstrated larger travel. It may be possible to suggest that this opposite behavior may be tied to particle shape where the small surface area particle has a significant length/diameter (L/D) ratio. However, close examination of the higher surface area orange raises the question that the respective L/Ds may be similar, just different in actual particle size.

The above approach is now used to examine the red products, all of which are PR254 with differing surface areas. The plots for the a* and b* data are seen in Figures 7 and 11, respectively. Comparison of the plots suggests that there is color travel for all three samples in green – red and the yellow – blue dimensions. Evaluation of the da*/dVA and the db*/dVA indicates that the travel in the b* dimension is greater with a db*/dVA = ~5 units and the da*/dVA = ~3 units. Both plots exhibit positive slopes. This is good with regards to the a* value indicating that the reds simply get more red without a specific travel in the undertone color. The larger db*/dVA is supportive of the idea that the reds travel from a blue shade red to a yellow shade red, as the b* value becomes

much larger. In a comparison of the da*/dVA and db*/dVB relative to the surface area, it is again seen that the larger surface area offers the lower degree of color travel. The difference, however, is small and may not differentiate the performance of the three products based on surface area.

The last comparison is between a variety of phthalo blue pigments, 15:1, 15:3, 15:4, and 15:6, with different particle sizes. The da* and db* plots are found in Figures 8 and 12 respectively. The b* plot does differentiate between the colors and offers generally parallel curves. The a* plot demonstrating the green – red shift that is characteristic of phthalo blues is clearly observed. In this instance, the sample with the second smallest surface area provides the least travel. This curve is relatively flat and offers a calculated da*/dVA = 0.51 units. It is particularly interesting to look closely at the da*/dVA for this sample. The value for this sample is 0.51 units suggest minimal color travel in the green – red dimension, a comparatively flat curve. Similarly, the sample with the largest surface area at nearly 80m2/g has a da*/dVA = 0.71 units. This suggests minimal travel and visually this is observed to be the case. Examination the a* plot for this product as though it is two plots divided at the 45-degree viewing angle provides a different view. A brief calculation of the da*/dVA from 45 to 110 degrees yields a value of about 1.5 units for this product nearly double the 0.7 units for the entire curve. This suggests a modest but identifiable green – red shift occurring above the 45-degree viewing angle. It can, however, still be stated that a larger surface area provides a smaller net color travel.

Conclusions:

A multi-angle spectrophotometer can be employed to evaluate the inherent color travel of pigment dispersions in a thermoplastic application.

Making use of the Lab* data and plotting against the viewing angle demonstrates the extent to which the color in question may travel.

Consideration of the pigment color in question provides the means to determine which color dimension provides the best opportunity to quantify the travel. A green – red travel would be seen in evaluation of the a* dimension, a yellow – blue travel would be seen by measuring the b* dimension.

A term has been developed, Equation #4, that expresses the average change in the color parameter in question in relation to the total degrees of viewing angle. This term is referred to the da*/dVA for green – red travel or db*/dVA for blue - yellow travel.

The above technique makes it possible to determine quantitatively the degree to which any given pigment may or may not experience color travel. Based on this evaluation it can be suggested that pigments that demonstrate <1.0 units exhibit minimal travel, >1 <3 moderate travel, and >3 units large travel. This may facilitate selection of pigments to improve visual color stability.

A relationship to a larger surface area (smaller particle size) and lower travel can be made. The relationship appears to be reversed for the orange products, suggesting that the relationship could be product- or chemistry-specific.

It is recommended that a multi-angle spectrophotometer be used whenever it is found necessary to identify and quantify the nature and extent of observed color travel. The use as a diagnostic tool may also then be expanded to quantify the exact nature of the color travel experienced.

The use of the above technique may facilitate pigment selection to provide visually color stable pigment selections when formulating for appearance.

Table 2 L* data

Pigment	Surface area m2/g	Dir.	-15°	15°	25°	45°	75°	110°	DL* (125°)	DL*/dVA
PY110	26.7	MD	85.16	68.66	59.91	52.41	51.18	51.84	-33.32	-2.67
		90°	80.56	67.73	58.95	52.64	50.93	51.36	-29.2	-2.34
PY110	8.6	MD	84.36	64.25	51.98	40.35	37.11	39.71	-44.65	-3.57
		90°	79.02	63.62	51.59	40.07	36.65	39.49	-39.53	-3.16
PY138	31.6	MD	88.86	79.17	70.12	64.55	64.23	64.94	-23.92	*1.91
		90°	86.99	76.54	69.43	64.7	64.28	64.95	-22.04	-1.76
PY138	9	MD	88.56	76.81	66.72	59.77	58.88	60.25	-28.31	-2.26
		90°	85.73	73.93	65.87	60.45	59.12	60.42	-25.31	-2.02
PO73	20.8	MD	81.52	65.10	55.34	47.86	45.89	38.11	-43.41	-3.47
		90°	75.22	63.94	54.68	47.57	45.87	38.12	-37.1	-2.97
PO71	81	MD	78.57	57.6	44.35	30.75	27.38	29.25	-49.32	-3.95
		90°	72.79	56.03	43.61	30.79	27.58	29.48	-43.31	-3.46
PR254	15	MD	78.06	61.08	49.58	40.64	38.28	37.07	-40.99	-3.28
		90°	72.46	59.74	49.01	40.45	38.26	37.06	-35.4	-2.83
PR254	13.5	MD	77.29	59.86	48.97	39.95	37.46	36.28	-41.01	-3.28
		90°	71.12	58.46	48.28	39.79	37.55	36.4	-34.72	-2.78
PR254	25	MD	77.64	60.1	50.1	41.52	39.24	38.11	-39.53	-3.16
		90°	72.31	59.49	49.92	51.5	39.24	38.12	-34.19	-2.74
15:4	79.5	MD	68.85	56.58	39.4	23.81	18.23	13.28	-55.57	-4.44
		90°	65.62	51.59	37.45	23.74	18.39	13.3	-52.32	-4.18
15:6	73	MD	69.08	57.92	40.96	25.48	19.73	14.19	-54.89	-4.39
		90°	66.71	52.07	38.27	25.07	19.69	13.74	-52.97	-4.23
15:1	61.1	MD	72.13	53.58	38.47	23.46	16.85	10.82	-61.31	-4.9
		90°	65.69	51.46	37.17	22.79	16.7	10.8	-54.89	-4.39
15:3	49	MD	72.07	52.15	36.49	18.27	10.43	8.45	-63.62	-5.09
		90°	65.32	50.16	35.50	18.21	11.09	9.35	-55.97	-4.48

Table 3 a* data

Pigment	Surface area m2/g	Dir.	-15°	15°	25°	45°	75°	110°	Da* (125°)	Da*/dVA
PY110	26.7	MD	12.9	15.5	17.9	20.9	22.8	25.4	12.5	0.99
		90°	13.	14.8	17.9	21.6	22.8	25	11.9	0.96
PY110	8.6	MD	13.9	13.4	14.5	15.6	16.2	20.3	6.34	0.51
		90°	15.3	13	14.3	15.5	16	20	4.69	0.38
PY138	31.6	MD	-7.8	-10.4	-12.8	-14.8	-14.6	-11.5	-3.66	-0.29
		90°	-8.1	-11.1	-13.1	-14.8	-14.6	-11.6	-3.42	-0.27
PY138	9	MD	-3.2	-4.5	-5.8	-7.3	-7.4	-5.5	-2.27	-0.18
		90°	-3.7	-5	-6.1	-6.9	-7.4	-5.6	-1.99	-0.16
PO73	20.8	MD	23	31.8	39.4	47.5	49.7	49.9	26.96	2.16
		90°	25.9	32.2	39.9	47.8	49.8	49.8	23.93	1.91
PO71	81	MD	17.6	19.3	21.9	26.3	30.2	36.2	18.57	1.49
		90°	19.9	19.6	22.4	27.1	30.7	36.5	16.61	1.33
PR254	15	MD	26.4	38.5	50.3	63	66.6	66.1	39.8	3.18
		90°	29.7	39.5	51	63.3	66.7	66	36.3	2.91
PR254	13.5	MD	25.2	37.3	48.2	60.5	64.39	64.1	38.9	3.11
		90°	28.8	38.3	49	60.8	64.3	63.9	35.1	2.81
PR254	25	MD	24.2	36	45.5	56.4	59.9	59.5	35.27	2.82
		90°	27	36.3	45.6	56.3	59.8	59.5	32.52	2.60
15:4	79.5	MD	-2.97	-2.7	-2.71	-3.66	-1.48	5.86	8.83	0.71
		90°	-3.17	-3.28	-3.09	-3.78	-1.61	6	9.17	0.73
15:6	73	MD	0.57	1.84	4	7.88	10.89	14.3	13.73	1.1
		90°	0.57	2.1	4.33	8.09	10.83	14.45	13.88	1.11
15:1	61.1	MD	-2.03	-1.07	-0.63	-0.23	1.04	4.35	6.38	0.51
		90°	-2.04	-1.43	-0.77	-0.10	1.03	4.38	6.42	0.51
15:3	49	MD	-1.68	0.46	2.86	9.42	17.47	19.90	21.58	1.73
		90°	-1.46	0.30	2.89	9.53	16.94	19.20	20.66	1.65

Table 4 b* data

Pigment	Surface area m2/g	Dir.	-15°	15°	25°	45°	75°	110°	Db* (125°)	Db*/dVA
PY110	26.7	MD	16.96	28.87	38.4	58.29	73.55	79.63	62.67	5.01
		90°	15.79	26.27	37.75	60.27	74.55	79.18	63.39	5.07
PY110	8.6	MD	13.53	20.08	26.82	40.36	53.73	62.47	48.94	3.92
		90°	14.27	18.47	25.18	40.48	53.85	62.31	48.04	3.84
PY138	31.6	MD	25.77	34.76	48.66	68.55	76.68	79.57	53.8	4.3
		90°	25.76	37.02	49.99	68.49	76.4	79.4	53.64	4.29
PY138	9	MD	26.21	33.23	45.52	66.4	76.95	81.57	55.36	4.43
		90°	25.28	34.62	46.59	67.23	76.87	81.48	56.2	4.5
PO73	20.8	MD	9.42	22.05	32.9	55.41	70.37	72.55	63.13	5.05
		90°	10.4	21.04	33.43	57.05	71.21	72.7	62.3	4.98
PO71	81	MD	3.51	10	13.31	23.22	35.34	42.82	39.31	3.14
		90°	3.81	9.18	13.49	24.54	36.37	43.44	39.63	3.17
PR254	15	MD	3.25	14.18	23.64	44.26	59.64	61.21	57.96	4.64
		90°	3.85	13.59	23.96	45.31	60.14	61.22	57.37	4.59
PR254	13.5	MD	3.22	13.92	22.43	41.37	56.25	58.16	54.94	4.4
		90°	3.94	13.41	22.95	42.25	56.12	57.71	53.77	4.3
PR254	25	MD	4.86	15.9	24.37	42.69	56.55	58.4	53.54	4.28
		90°	5.86	15.37	24.27	42.78	56.82	58.96	53.1	4.25
15:4	79.5	MD	-18.45	-18.57	-24.07	-33.05	-36.97	-36.44	-17.99	-1.44
		90°	-20.26	-20.92	-25.21	-33.24	-37.05	-36.53	-16.27	-1.30
15:6	73	MD	-25.66	-27	-34.56	-46.55	-48.6	-44.83	-19.17	-1.53
		90°	-28.08	-30.96	-36.7	-46.11	-48.62	-44.31	-16.23	-1.3
15:1	61.1	MD	-18.86	-20.63	-26.09	-35.29	-38.52	-34.72	-15.86	-1.27
		90°	-21.28	-22.5	-27.07	-35.81	-38.75	-34.77	-13.49	-1.08
15:3	49	MD	-14.88	-13.10	-16.88	-25.11	-33.04	-35.32	-20.44	-1.64
		90°	-16.28	-14.47	-17.48	-25.37	-32.74	-34.92	-18.64	-1.49

Figure 1

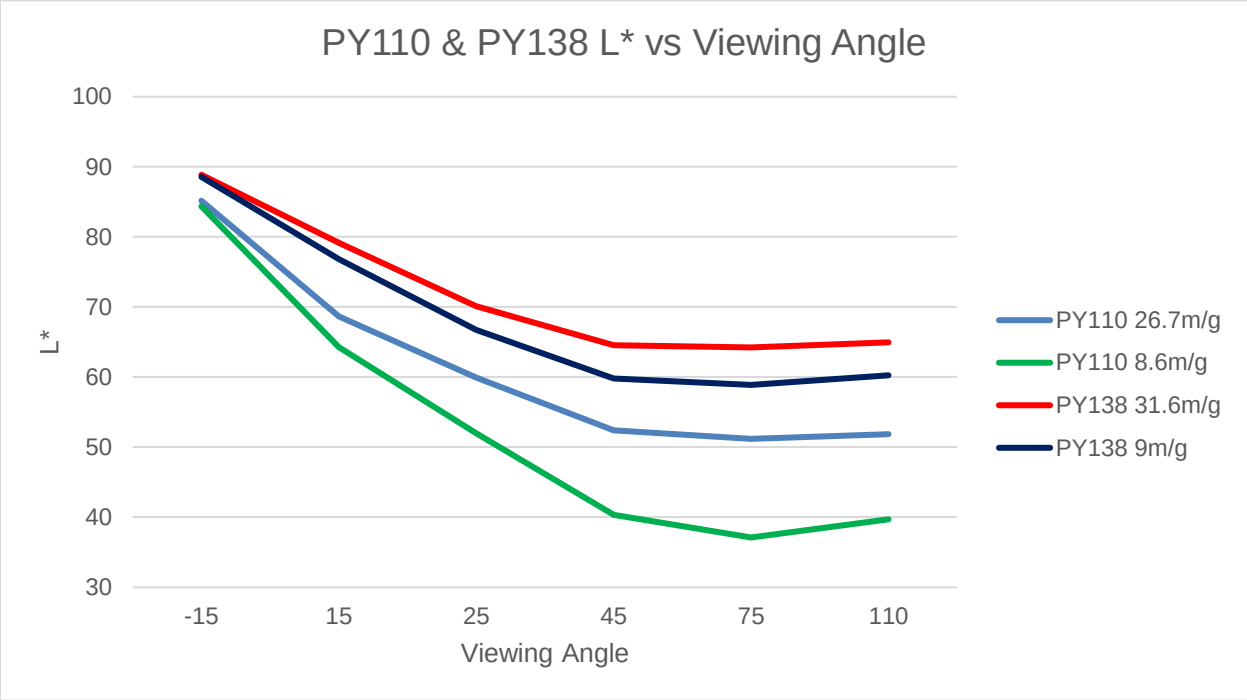


Figure 2

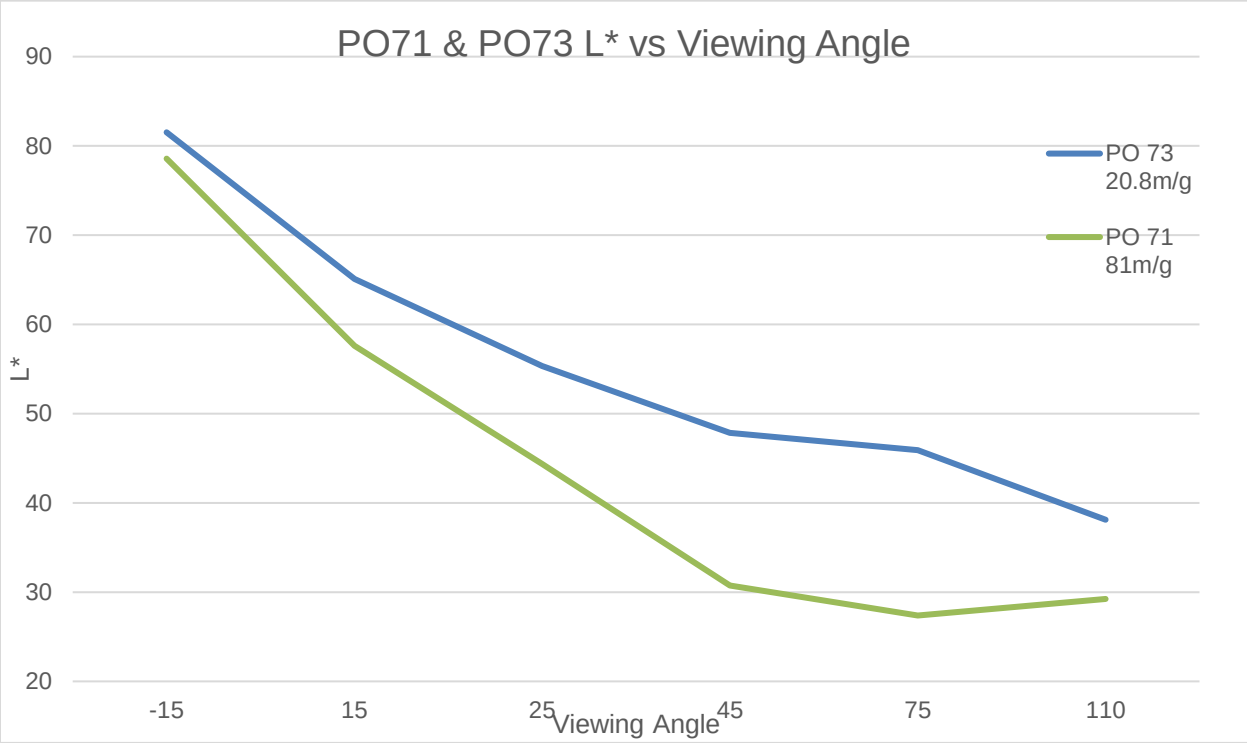


Figure 3

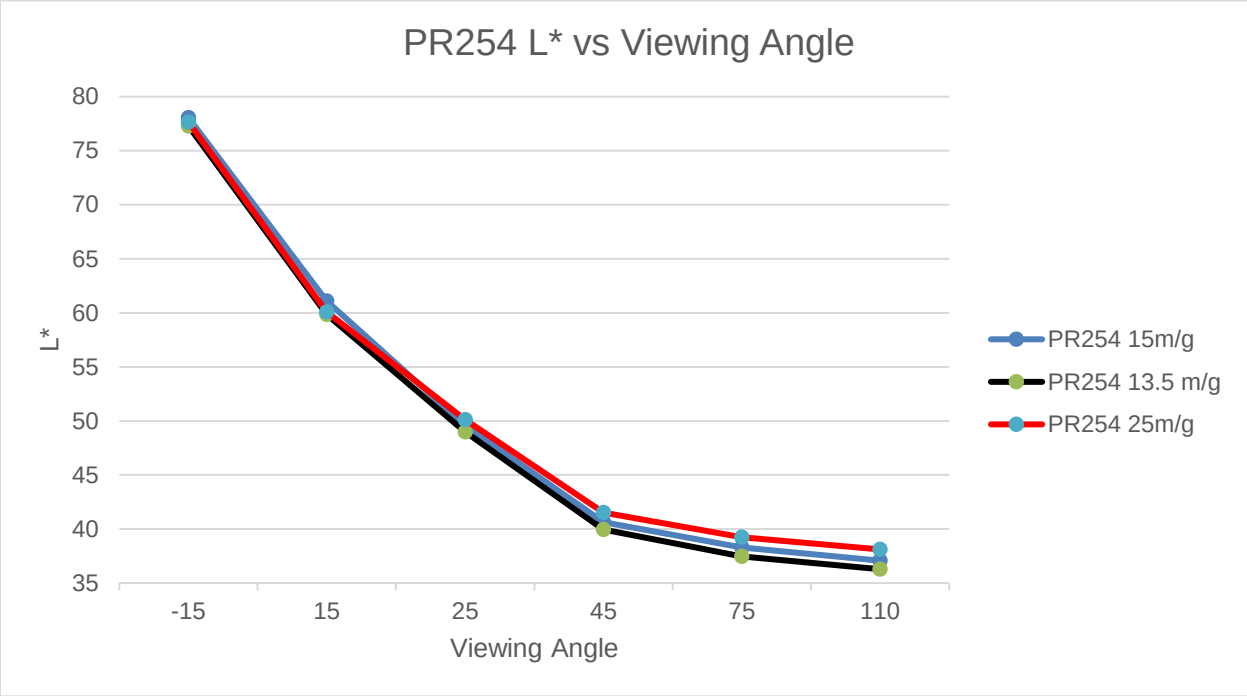


Figure 4

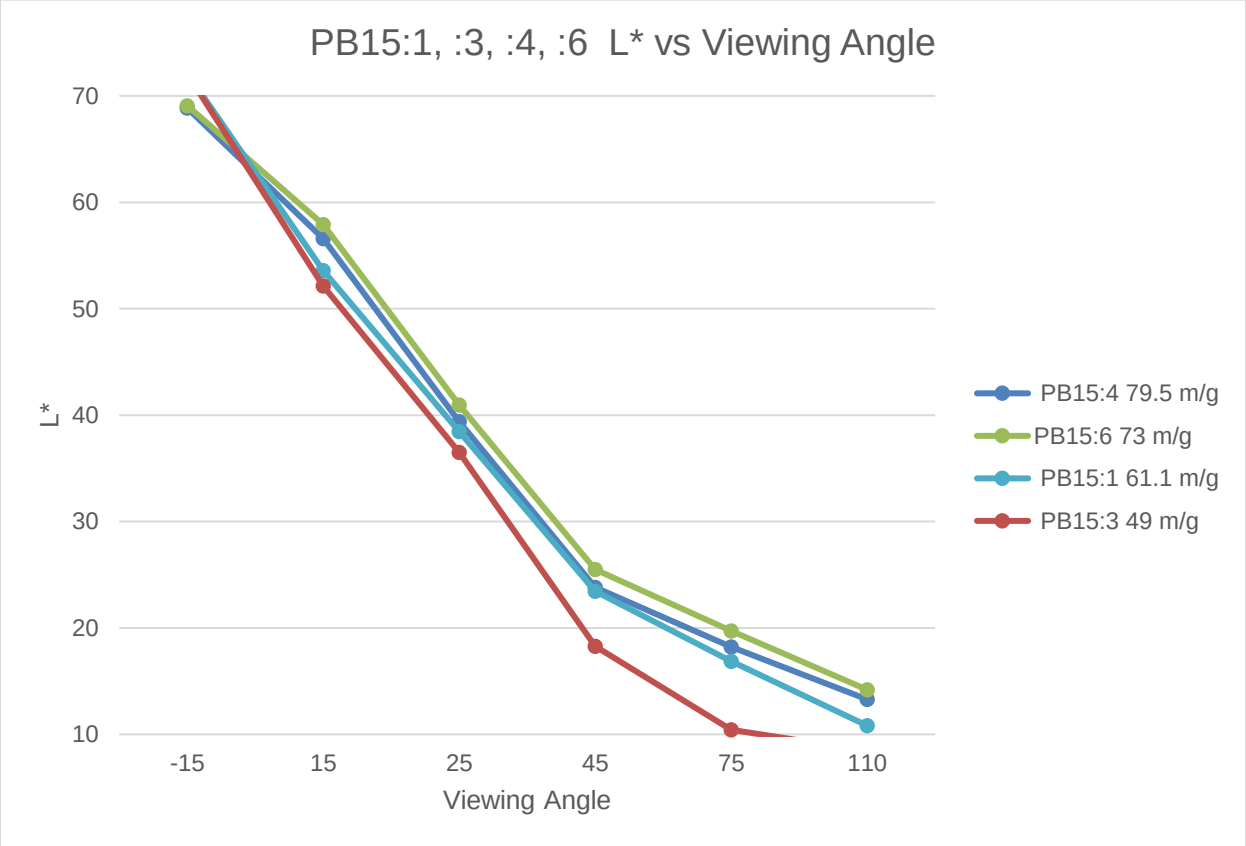


Figure 5

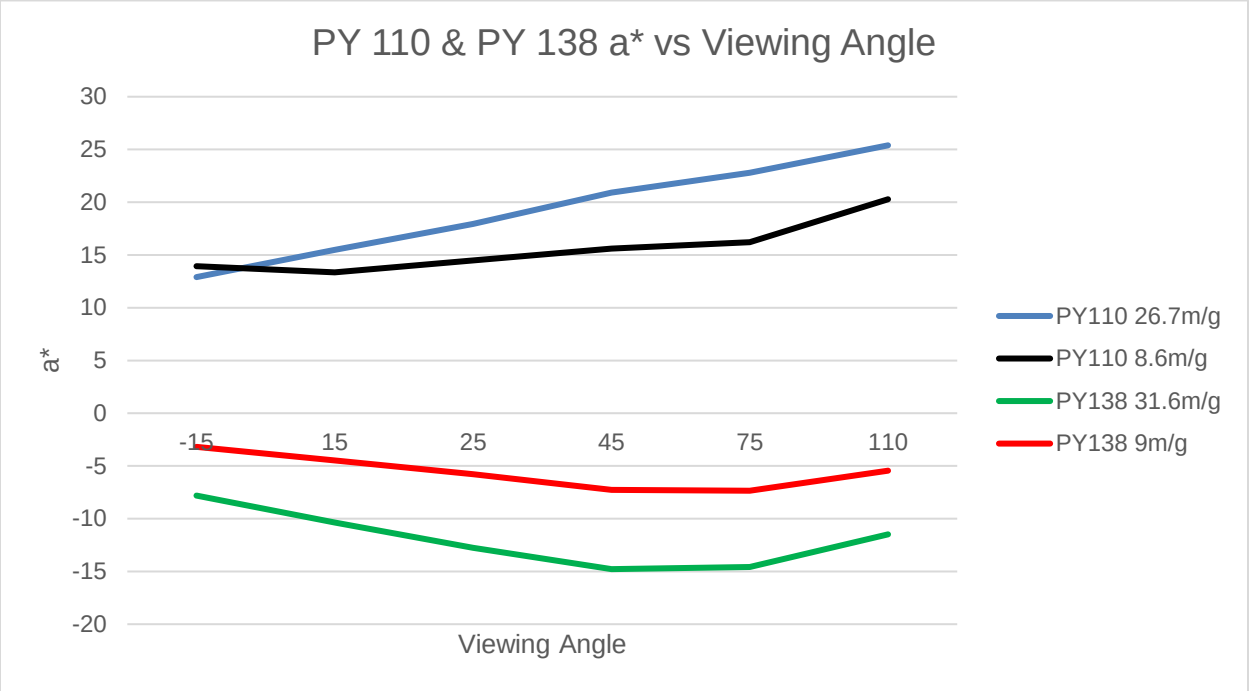


Figure 6

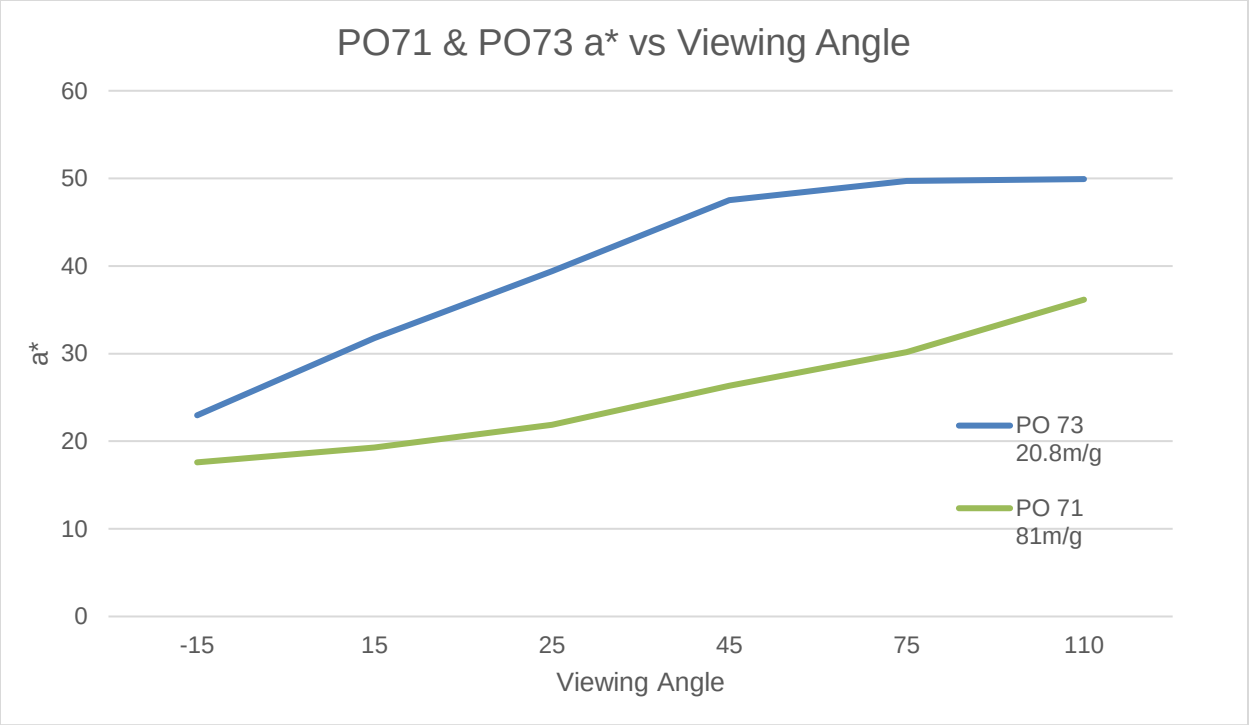


Figure 7

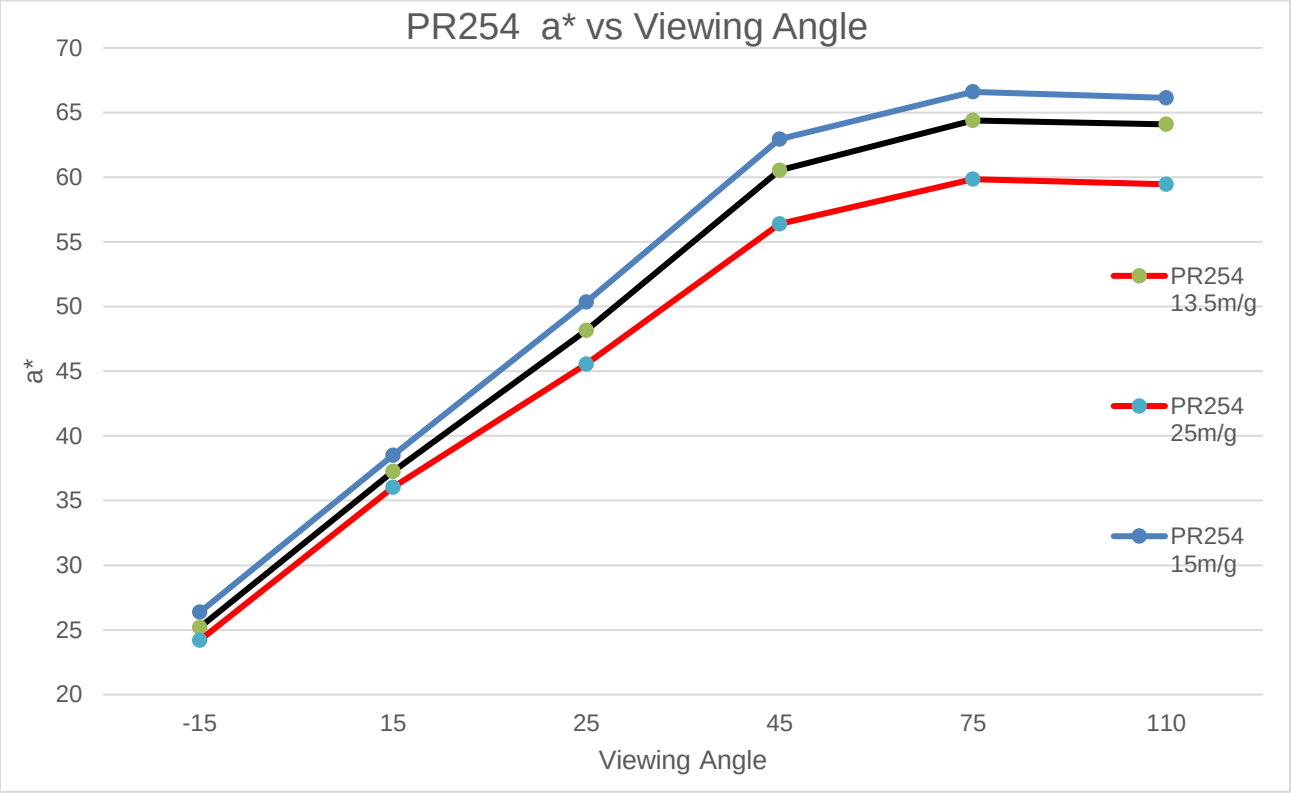


Figure 8

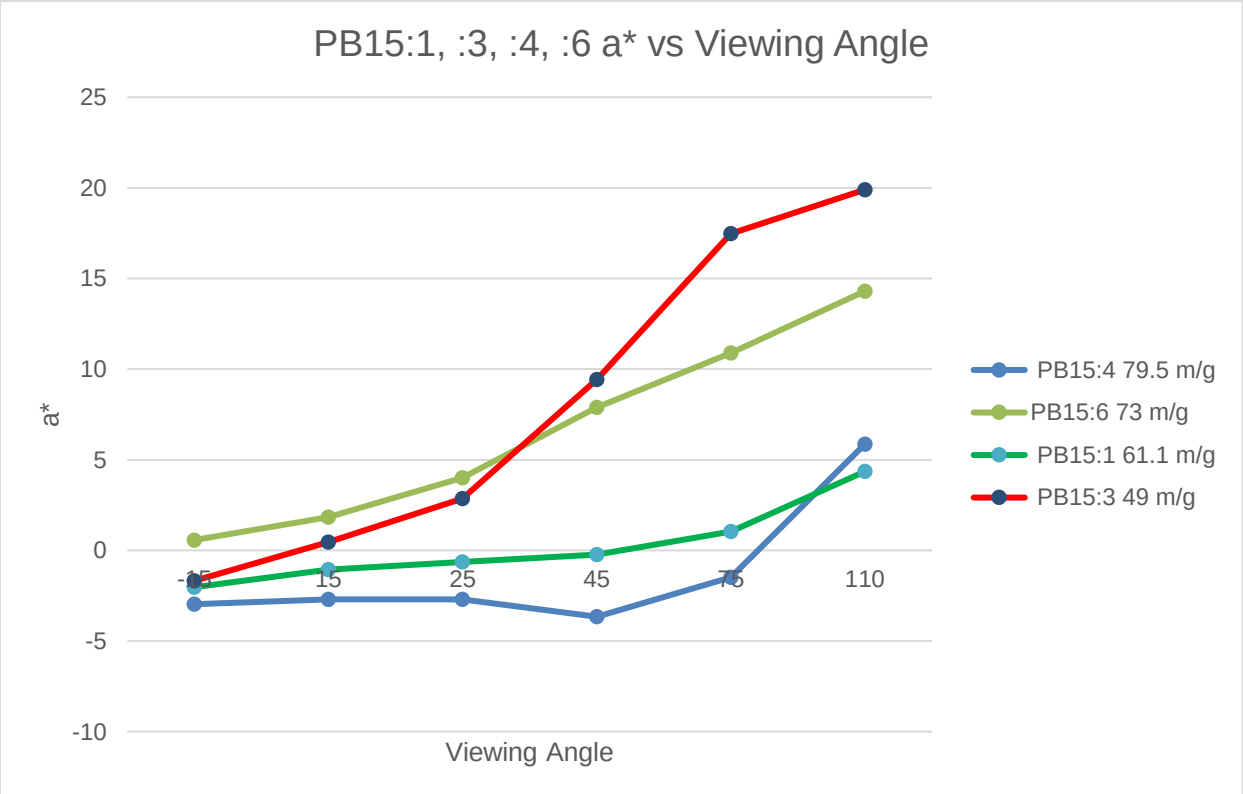


Figure 9

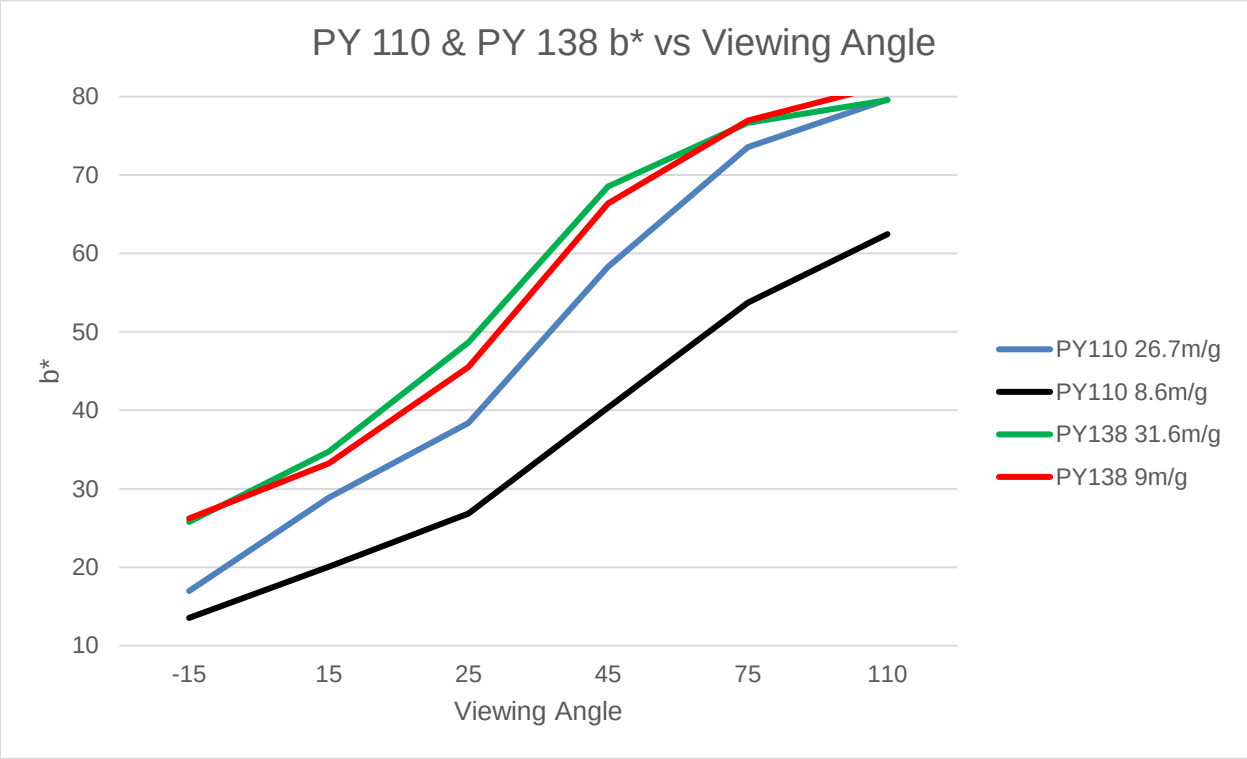


Figure 10

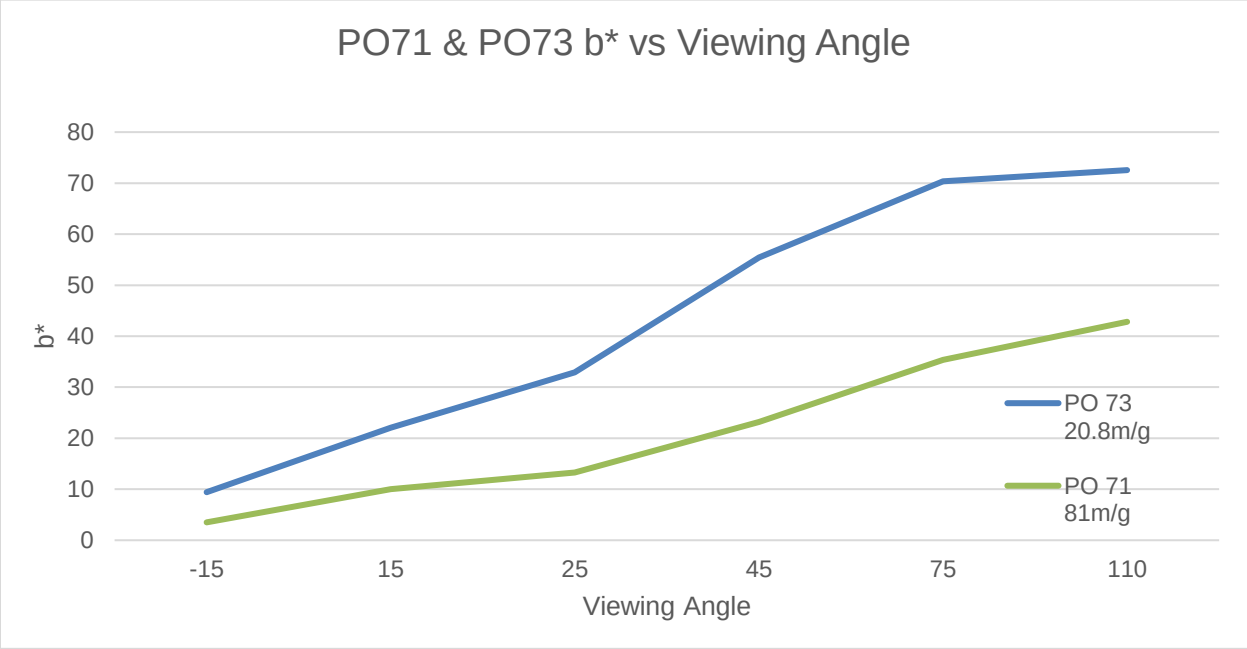


Figure 11

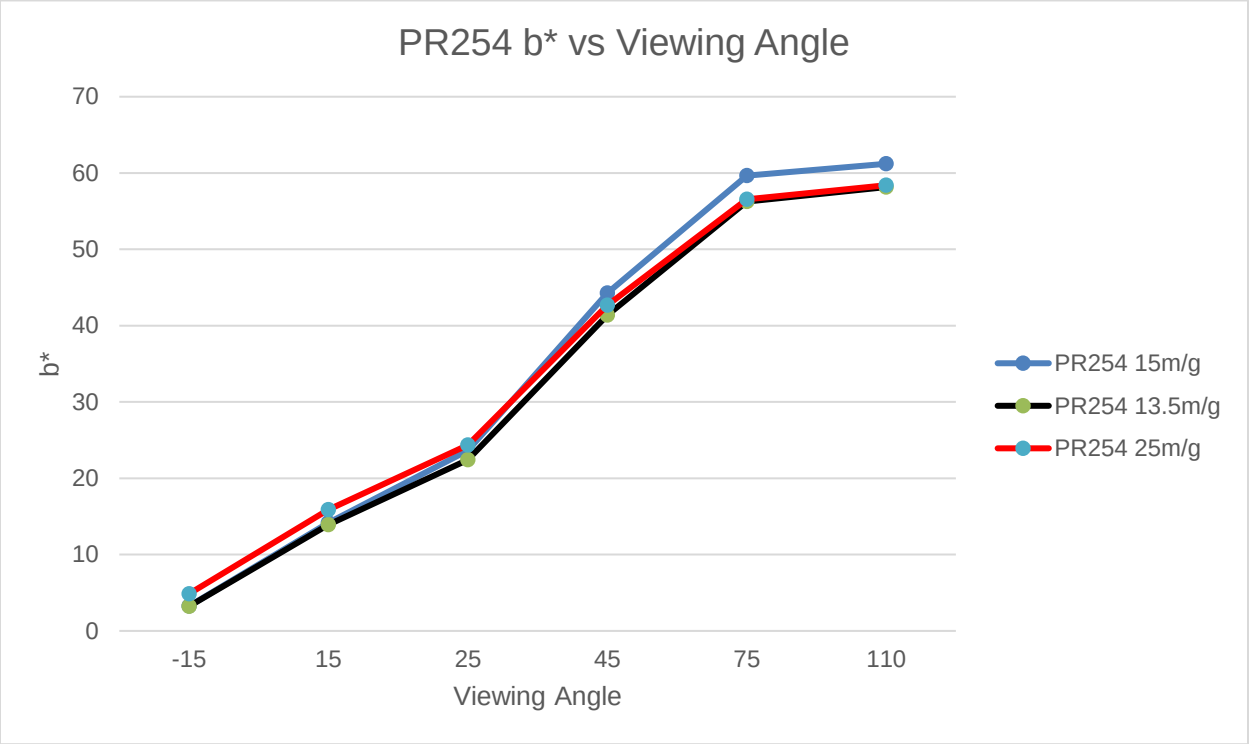
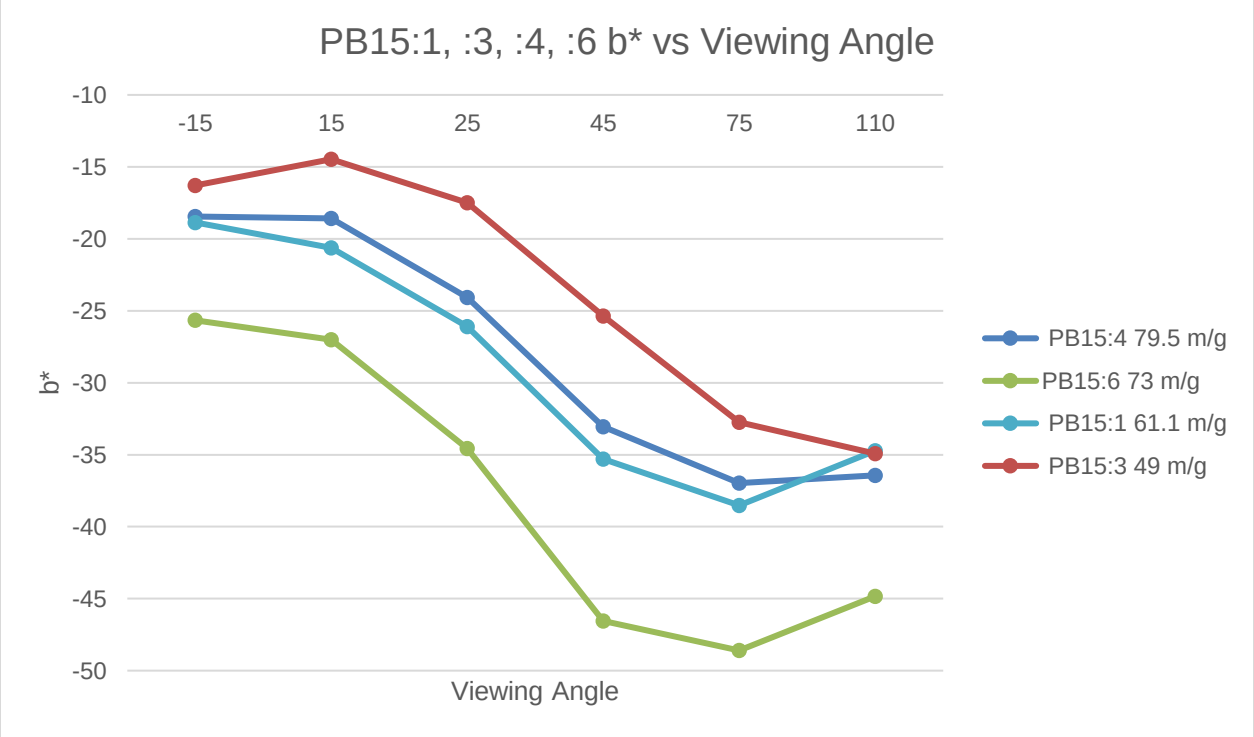
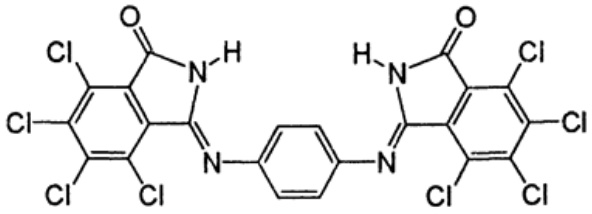


Figure 12

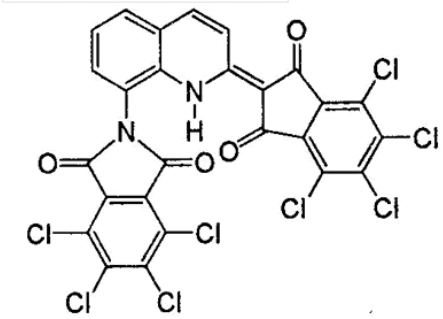


APPENDIX I

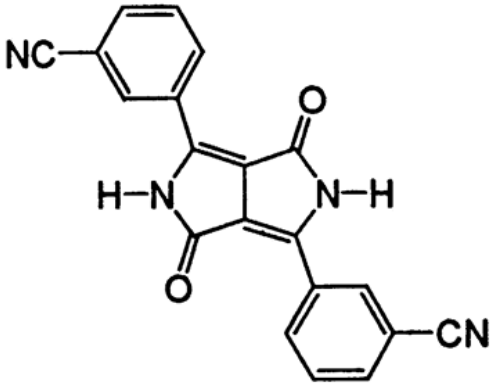
Pigment Yellow 110, isoindolinone



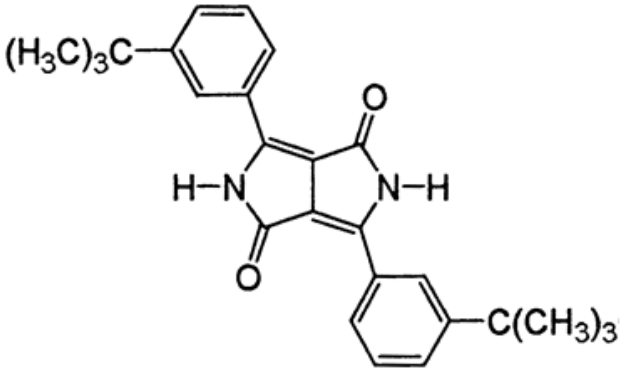
Pigment Yellow 138, quinophthalone



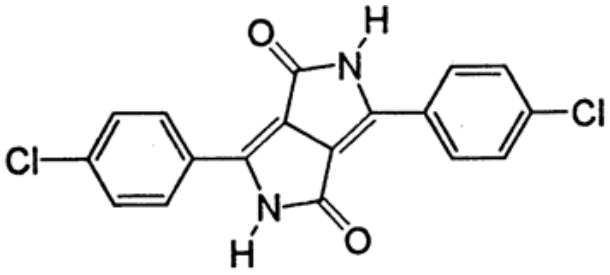
Pigment Orange 71, DPP, dicyano



Pigment Orange 73, DPP, dibutyl



Pigment Red 254, DPP, dichloro,



Pigment Blue 15:1, :4, :6, PCN