23 Years of Measurement Standardization for Effect Finishes . . .

Problems, Progress, Promise

Larry E. Steenhoek, DuPont Engineering R&D

March 6, 2012

Detroit Colour Council

A Little History

1935 First metallic automotive paints

1964 First batch of metallic paint instrumentally shaded

1987 First presentations of 3-angle measurement of metallic finishes (ISCC Williamsburg Conf.)

- D. H. Alman “Directional Measurement of Metallic Flake Finishes”
- W. H. Venable “A Model for Interpreting Three-Angle Measurements of Flake Finishes”
- L. E. Steenhoek “Goniophotometry as an Appearance Research Tool”

1988 First use of portable 3-angle instrument on automotive production line

1989 ASTM Task-Force E12.03.02 (now E12.12) on “Metallic and Pearlescent Color” chartered

2001 First DIN standard (DIN 6175-2) on tolerances for gonioapparent automotive paints

2003 First ASTM standard (E-2194) “Multiangle Color Measurement of Metal Flake Pigmented Materials”

2008 ASTM standard (E-2539) “Multiangle Color Measurement of Interference Pigments”

Subcommittee Scope E-12.12 Gonioapparent Color

This committee will study the color measurement of gonioapparent materials (e.g., those containing metallic and interference pigments) looking at quality control aspects, not colorant formulation and shading. Specifically, our scope will be :

1. Instrumental Measurement

- Correlation with observer response
- Measurement efficiency - most information with the least number of measurements
- Calibration
- Specimen preparation
- Specimen presentation
- Precision, bias and repeatability
- Instrument characteristics

2. Expression of Measurement Results

- Color metric (CIELAB, CMC, etc)
- Appearance attributes

3. Interpretation of Data

- Relative importance of angles
- Modeling

4. Recommended Procedure for Setting Tolerances and Evaluating Compliance

False Starts & Unexpected Places

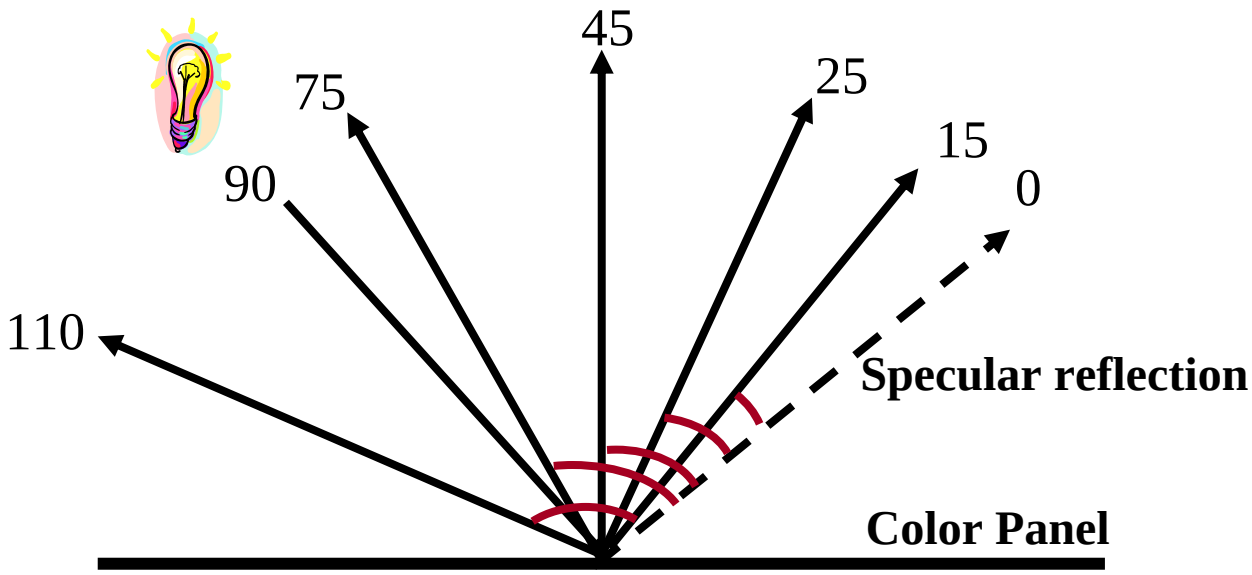
Common Lexicon – Addition of new section to ASTM E284 containing 73 terms pertaining to gonioapparent phenomena

- Gonioapparent, *adj* – pertaining to change in appearance with change in illumination angle or viewing angle.
- Aspecular, *adj* – of angles, measured with reference to the specular direction
- Color Angle**,** *n—in measurement of gonioapparent phenomena*, half the angle between the illumination and detection axes of the measurement geometry.

Standard Practice for Specifying the Geometry of Multiangle Spectrophotometers

Multiangle White Calibration Standard – NIST SRM 2017

Metallic Colors and the Concept of Aspecular Angle



Determination of Optimum Geometry for Metallic Colors

D.H. Alman (DuPont) Model based on 36 metallic panels measured at 6 different aspecular angles

Model Order	Model Name	# of Meas. Directions	Avg. Res. S. S.
1	Linear	2	529
1	Linear	6	210
2	**Quadratic**	**3**	**12.5**
2	Quadratic	6	8.2
3	Cubic	6	0.6

Geometry Confirmation

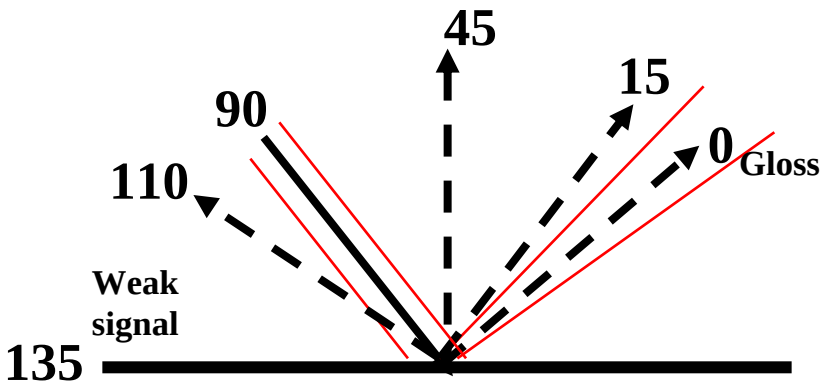
Mean Residual Sum of Squares

	All 22 Angles	15, 45, 110 DuPont Preferred Geometry	20, 45, 70 Alt. Geometry
Metallics (lightness) (18 panels)	4.01	**6.06**	18.20
Pearls (lightness) (16 panels)	3.90	**5.18**	12.05
Pearls (chroma) (16 panels)	2.08	**3.62**	8.92

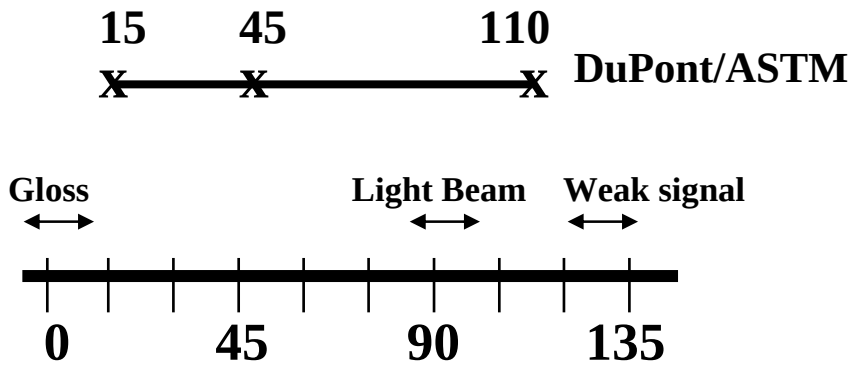
Measurement Angle Selection

The measurement system considers five factors:

Measurement Geometry

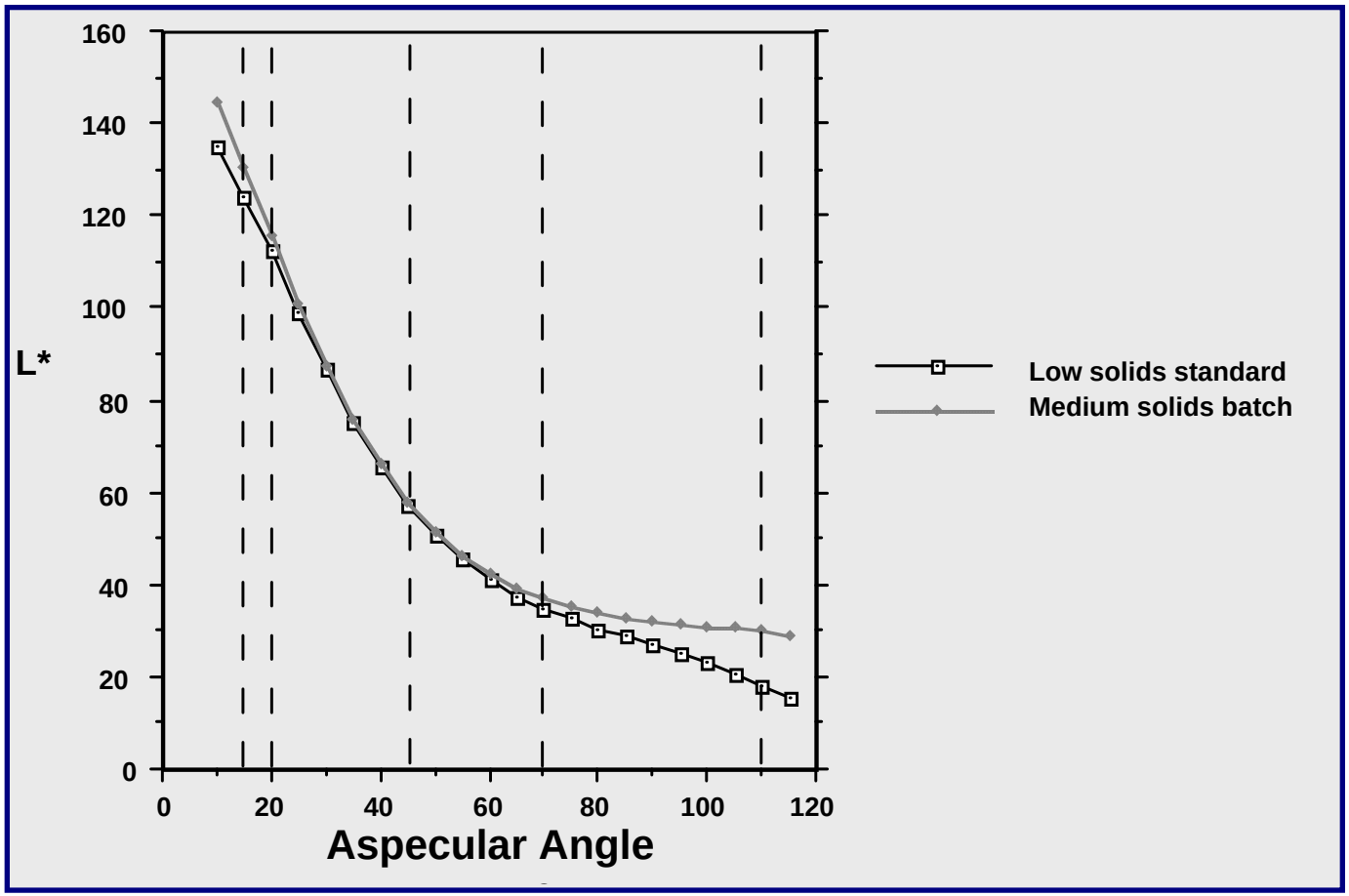


Aspecular Angles



Gloss	Avoid the gloss reflection at angles near 0.
Light Beam	Avoid the light source beam at angles near 90.
Weak signal	The reflection intensity is weak at very high aspecular angles.
Range	Select two angles with widest possible range (15, 110).
Standards	Set the middle angle at 45. This is the only angle with international material and documentation standards.

Metallic Color



Recommendation: For critical applications use as15, as45, as110 and make sure surface texture is the same standard to batch

International Standards for Measurement of Metal Flake Pigmented Materials

ASTM E 2194-03

- Recommended Geometry
  - 45:-30(as15), 45:0(as45), 45:65(as110)
- Alternates
  - 45:-25(as20), 45:-20(as25) instead of 45:-30(as15)
  - 45:25(as70) instead of 45:65(as110)

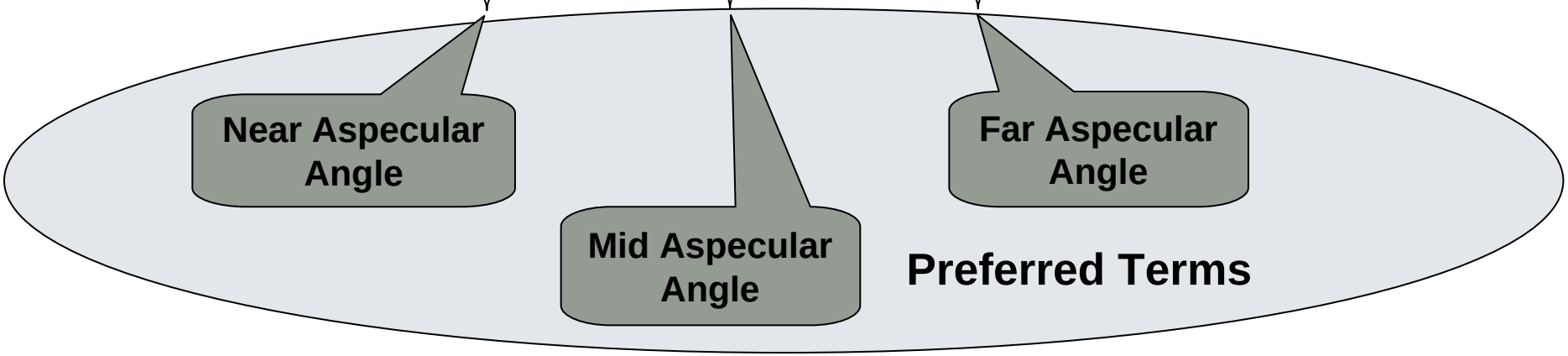
DIN 6175-2

- Recommended Geometry
  - 45:-20(as25), 45:0(as45), 45:65(as110) or 45:30(as75)

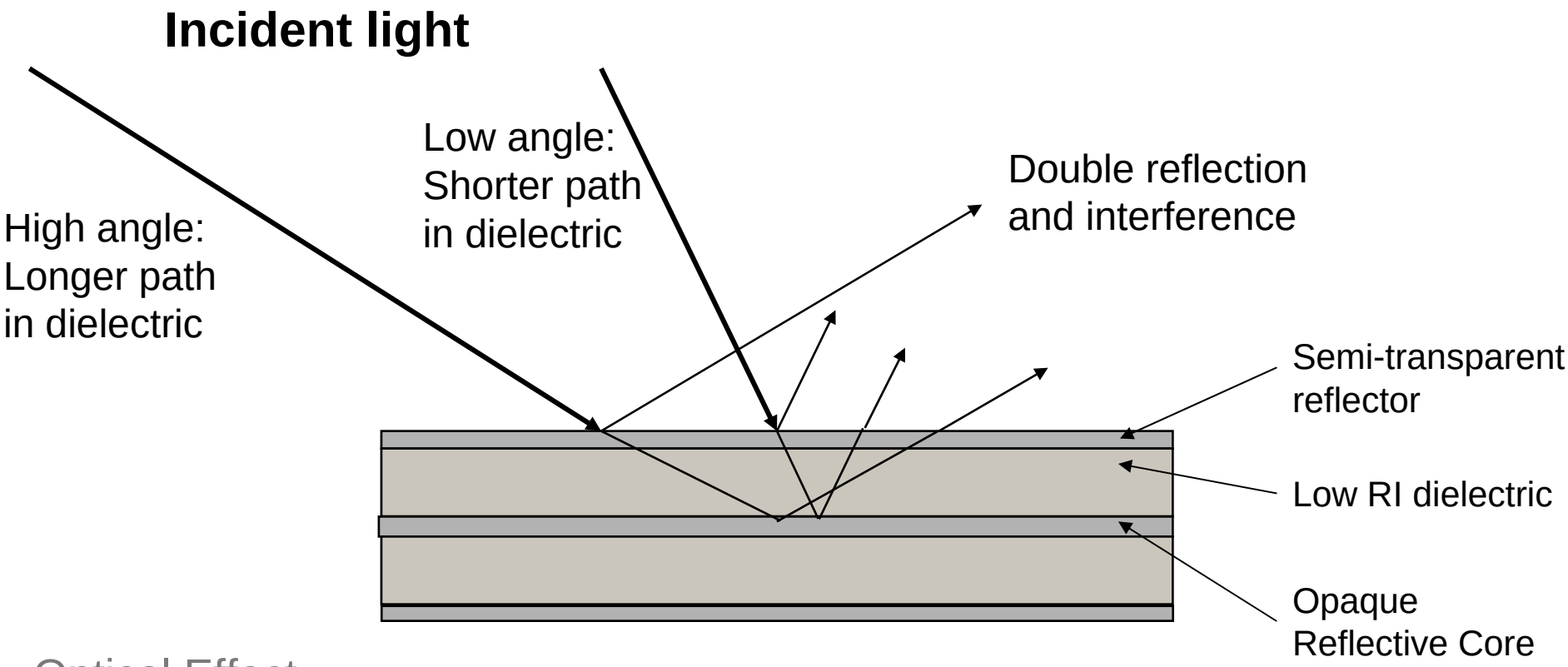
International Standards for Measurement of Metal Flake Pigmented Materials

ASTM E 2194-03

- Recommended Geometry
  - 45:-30(as15) 45:0(as45) 45:65(as110)



Interference Flake Pigments



Optical Effect

- Opaque, interference color in reflection

Visual Effect

- Intense specular interference color with up to 270° hue shift depending on viewing angle

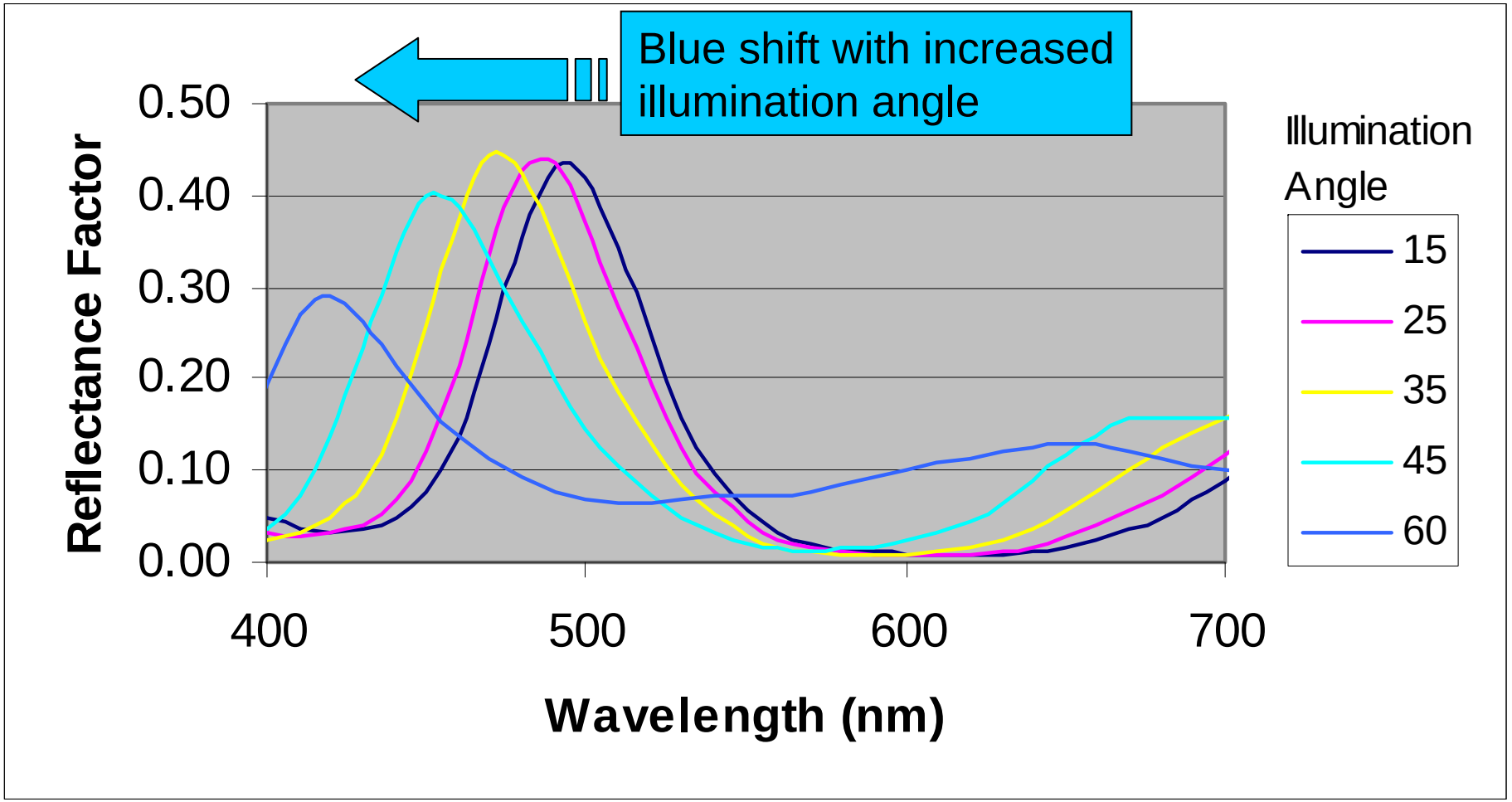
Interference Flake Pigments

For a given measurement geometry, any hue shift effect occurs only from flake oriented as specular reflectors of the illumination source to the detector

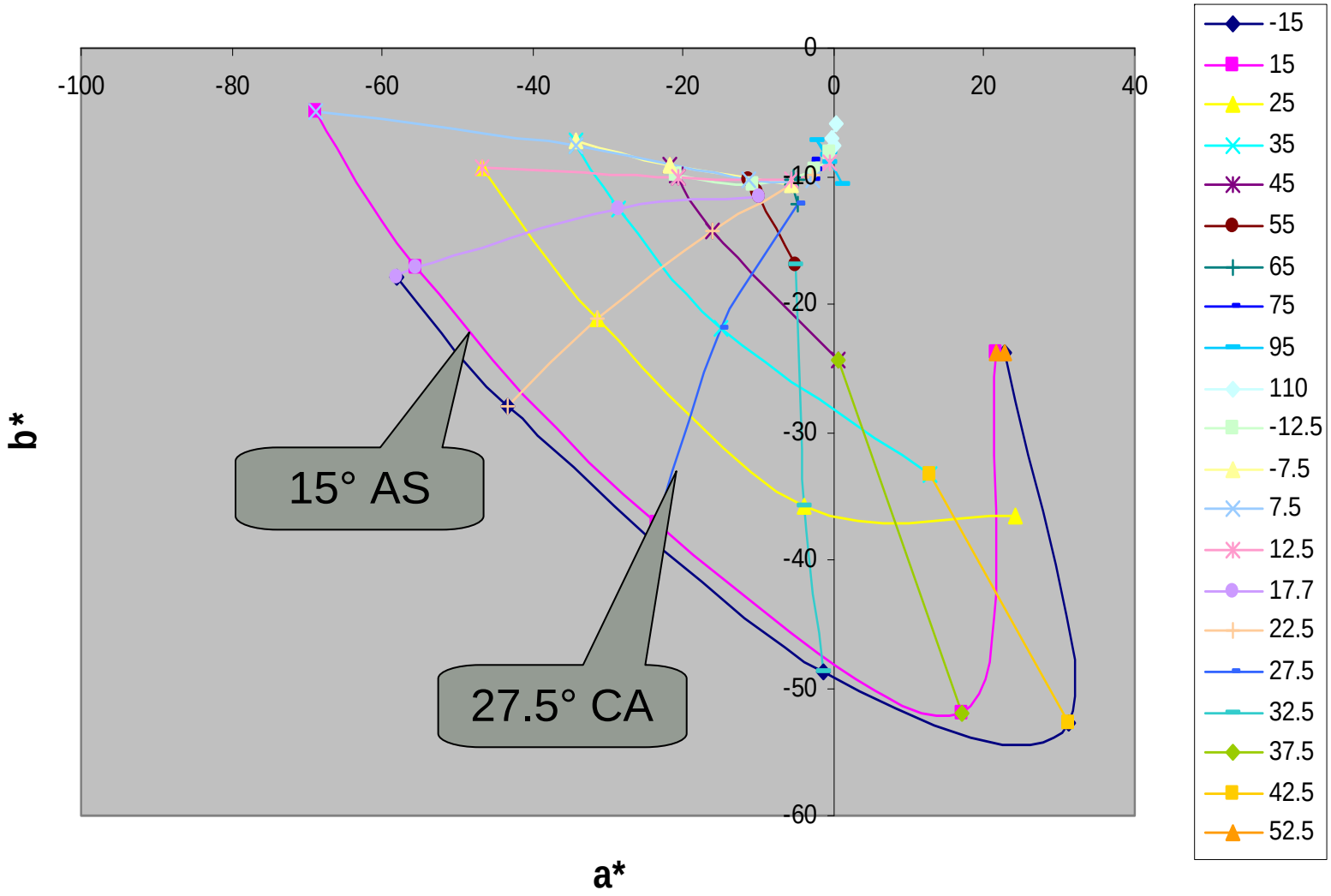
Color Angle *(illumination angle from "flake" perspective, 0.5* included angle between illumination and view)* **and makeup of interference layer (R.I. & thickness) determines hue shift**

Flake orientation and surface morphology determine lightness variation (flop) and are characterized by measurements taken at different aspecular angles. (Similar behavior to that of metal flake pigments)

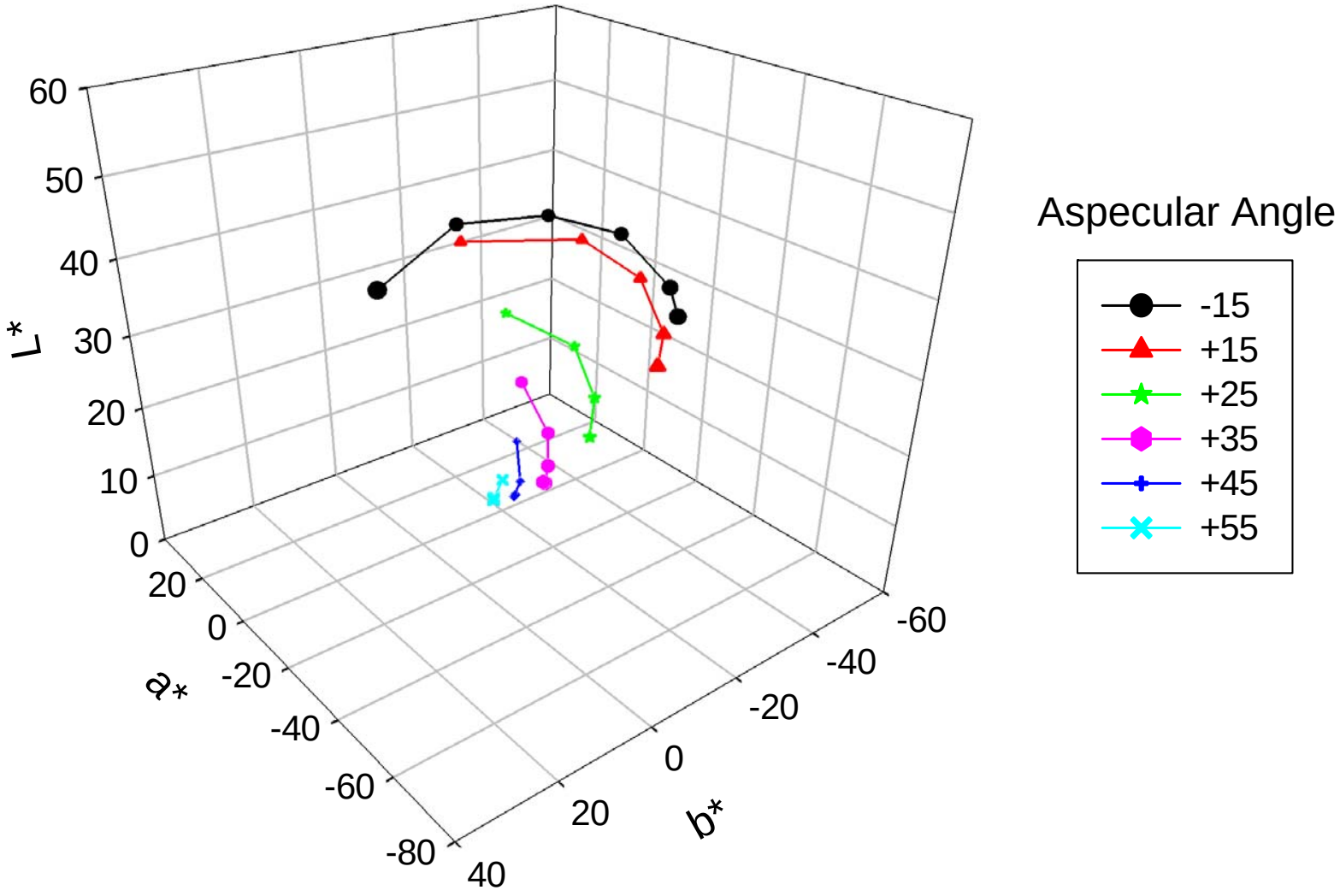
Ford Mystichrome @ 15° Aspecular



Ford Mystichrome



Ford Mystichrome



Recommended Angles for Multiangle Measurement of Interference Pigments per ASTM E2539

Specified Angles for Measuring the Color Range Due to Interference

Illumination Angle	Detection Angle	Aspecular Angle	Designation
45°	-60°	-15°	45° : -60° (as-15) (ca 52.5)
45°	-30°	+15°	45° : -30° (as 15) (ca 37.5)
15°	-30°	-15°	15° : -30° (as-15) (ca 22.5)
15°	0°	+15°	15° : 0° (as 15) (ca 7.5)

Color Angle

Specified Angles for Measuring the Color Due to Scattering or Orientation

Illumination Angle	Detection Angle	Aspecular Angle	Designation
45°	**-30°**	**15°**	**45° : -30° (as 15)**
45°	-20°	25°	45° : -20° (as 25)
45°	**0°**	**45°**	**45° : 0° (as 45)**
45°	30°	75°	45° : 30° (as 75)
45°	**65°**	**110°**	**45° : 65° (as 110)**

Geometries in **BOLD** are preferred

Future Standardization

What about routine QC of paint materials containing interference flake?

Question:

ASTM standard E2539 describes the measurements required to characterize the color behavior of the hue shifting pigments.

Are the same measurements required for control of materials (colors) containing mixtures of these pigments with absorbing and scattering pigments once the pigmentation is known?

Important to:

- Pigment Users (e.g. paint companies)
- End-Product Manufacturers (e.g. auto companies)

Experimental Design

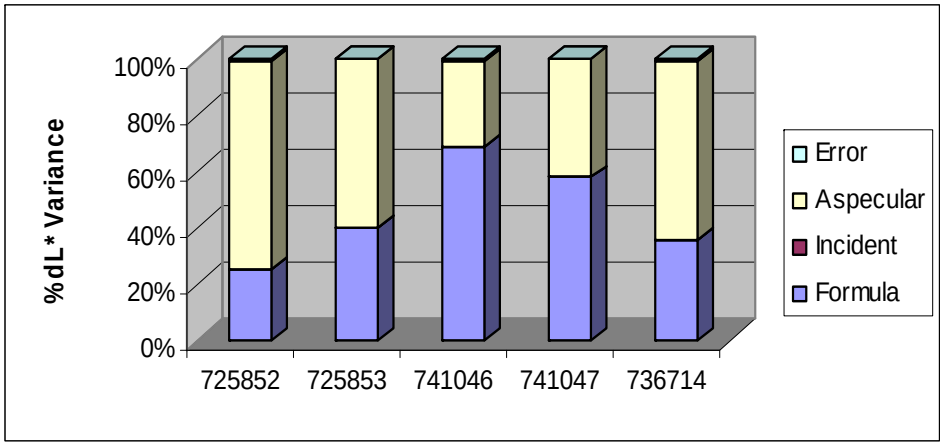
- Select a set of production colors containing mixtures of interference flake pigments with absorbing and scattering pigments
- Prepare a series of color difference panels by increasing the concentration of each of the pigment components in the formula one at a time. (i.e. 5 pigments > 6 panels)
- Measure the series of prepared panels at a wide variety of angles of illumination and detection.
- Perform nested ANOVA analysis on both absolute color and color difference data to determine source and statistical significance of sources of variance.

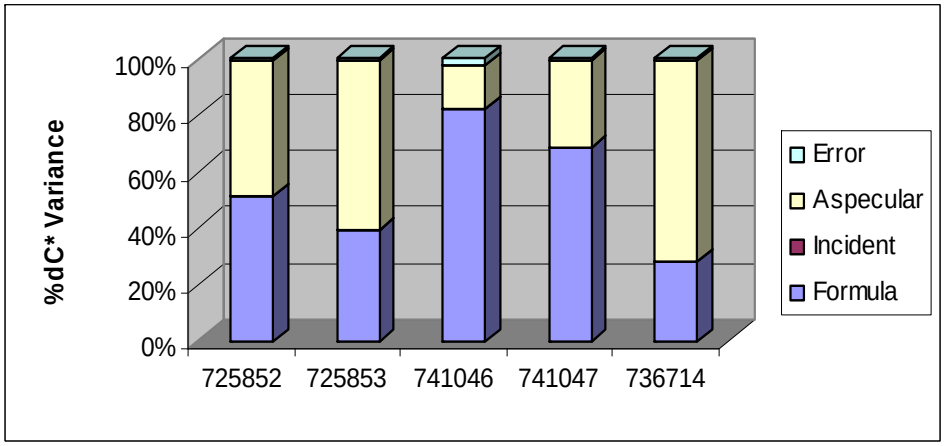
Measurement Matrix

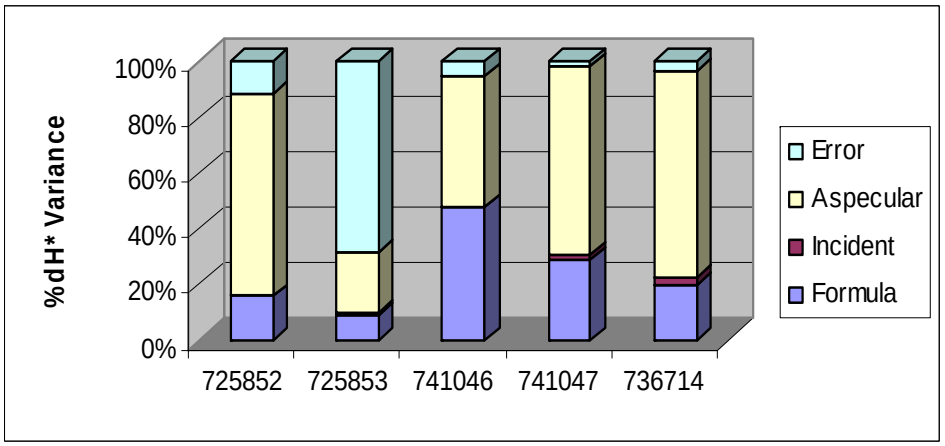
Illumination Angle \ Aspecular Angle	-15	15	25	35	45	55	65	75	95	110
10	X			X	X	X	X	X	X	
15	X	X			X	X	X	X	X	
25	X	X	X	X			X	X	X	X
35	X	X	X	X	X	X			X	X
45	X	X	X	X	X	X	X	X		X
60	X	X	X	X	X	X	X	X	X	

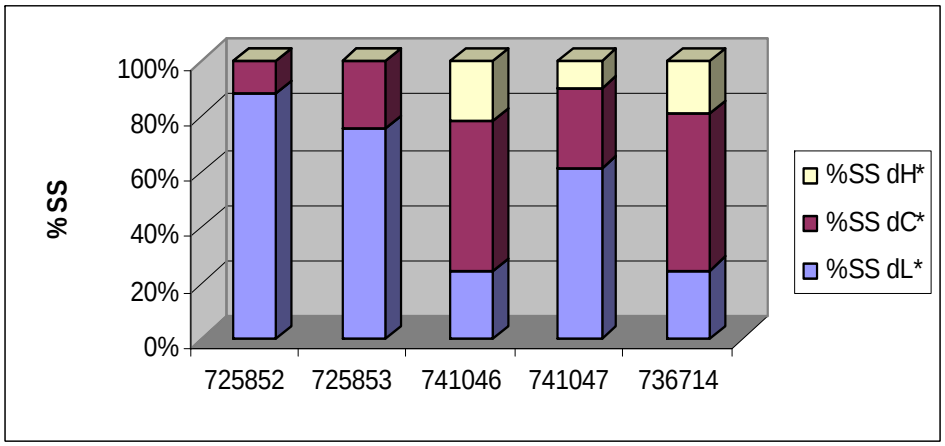
Measurements courtesy Mike Nofi, Flex Products

Color Difference for Specimens Containing Hue Shifting Interference Pigments









	725852			725853			741046			741047			736714		
	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*
Formula	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Formula * Incident	0.9992	0.8328	0.9983	0.9995	0.9856	0.3804	1.0000	0.7832	0.9957	1.0000	0.9999	0.2836	1.0000	0.9970	0.1061
Aspecular (Incident)	0.8666	0.2336	0.3528	0.8889	0.2816	0.2382	1.0000	0.9999	1.0000	0.0183	1.0000	0.0580	0.1882	0.0579	0.8693
Incident	0.9666	0.4147	0.7439	0.9716	0.8431	0.3046	0.6503	0.8523	0.8866	0.9535	0.5351	0.1796	0.9771	0.9446	0.7679
Formula*Aspecular(Incident)	<.0001	<.0001	<.0001	<.0001	<.0001	0.0007	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001

Hue Shifting Pigments: (tentative recommendation)

Pigment identification & manufacturing

- Microscopic analysis
- Use multi-illumination geometry per ASTM E 2539

Shading and control of colors containing hue shifting pigments combined with other pigments

- 3-angle aspecular geometry per ASTM E 2194-03 or DIN 6175-2

Future Standardization (cont.)

Color difference and gonioapparent materials

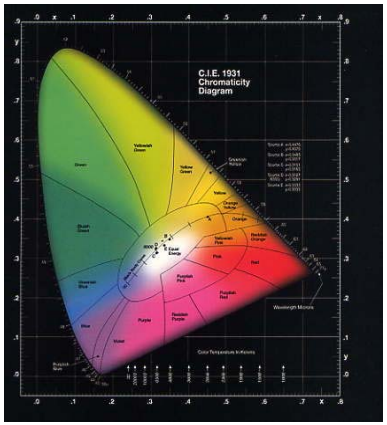
- All existing dE equations are based on solid colored samples
- What is the best dE equation for this class of materials?

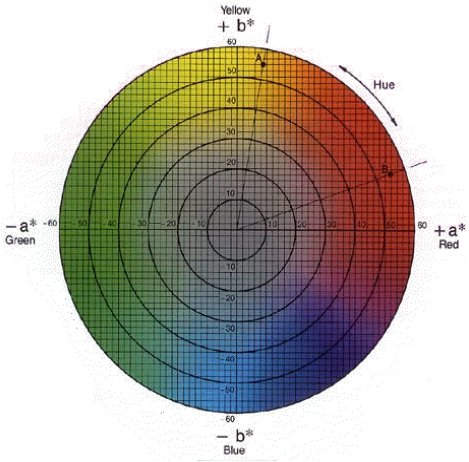
Visual evaluation

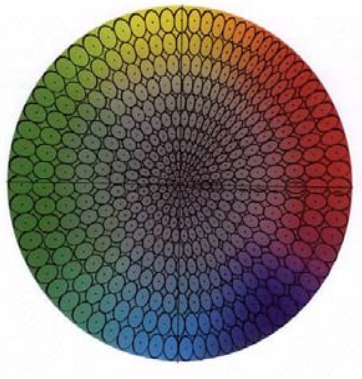
- New ASTM E12.12 Task group forming to study

New technologies F.Y.I.

Color Difference Equations







CIE Chromaticity

CIELAB

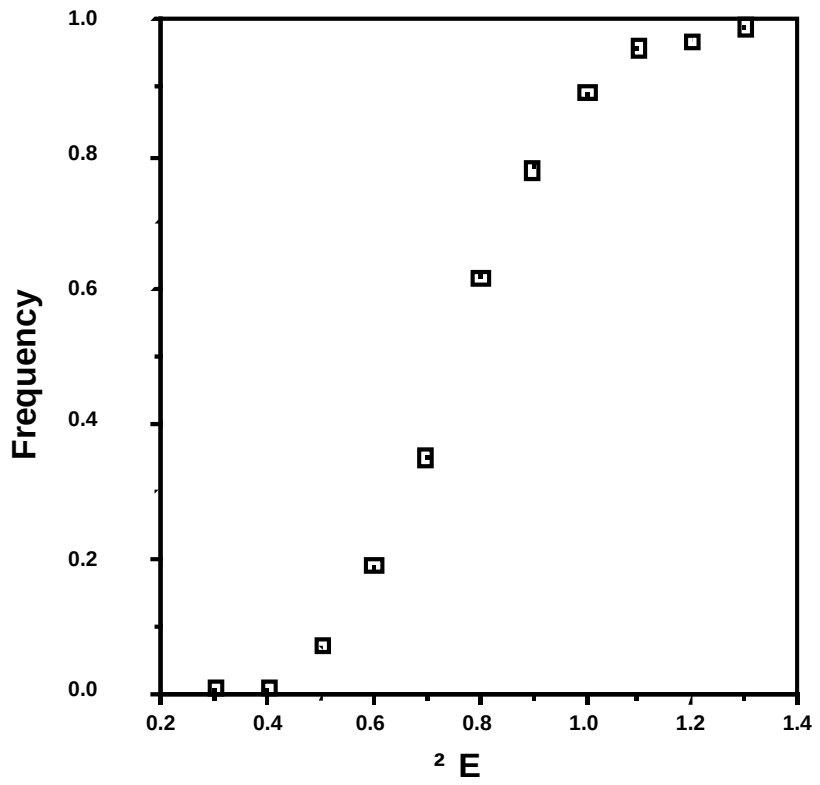
CMC/CIE94/DE2000

$$\Delta E = \left[\left(\frac{\Delta L^*}{K_L S_L} \right)^2 + \left(\frac{\Delta C^*_{ab}}{K_C S_C} \right)^2 + \left(\frac{\Delta H^*_{ab}}{K_H S_H} \right)^2 \right]^{0.5}$$

Resulted from databases of visual observations of solid color differences

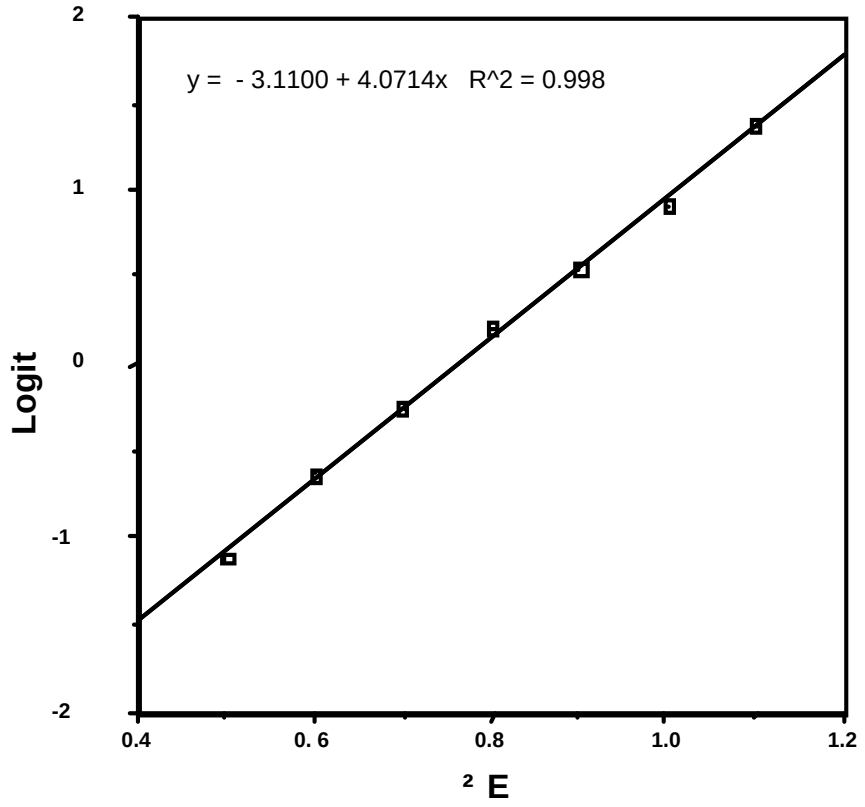
Logit Analysis

Typical frequency of rejection versus color difference



Logit function linearizes region of interest

Logit = log f/(1-f)



Almost everyone accepts low ΔE pairs
Everyone rejects high ΔE pairs

Logit linearizes a normal distribution allowing determination of a tolerance, ΔE at a reasonable acceptance rate (e.g. 50%)

Experimental Design

- Colors studied: Light Silver, Medium Silver and a Dark Silver
- Color difference panels prepared by additions of black
- ⇨Differences in lightness only, changes in hue, chroma negligible.
- Color differences measured at aspecular angles of 15˚, 25˚, 45˚, 75˚, 110˚ ⇨ providing 15 color centers:

SERIES	15º	25º	45º	75º	110º
Light	140.33	103.40	57.15	37.77	33.64
Medium	130.76	93.75	48.69	28.29	22.37
Dark	78.66	51.72	24.17	11.42	6.80

- 30 observers; respond “Yes” or “No” to the question
- “Is this an acceptable color difference?”
- Logit of the frequency of rejection was plotted against ΔL^* for each color center. Logit = log[(1-f)/f], where f = frequency
- ΔL^* at a frequency of 50% (logit = 0) was taken as the tolerance.

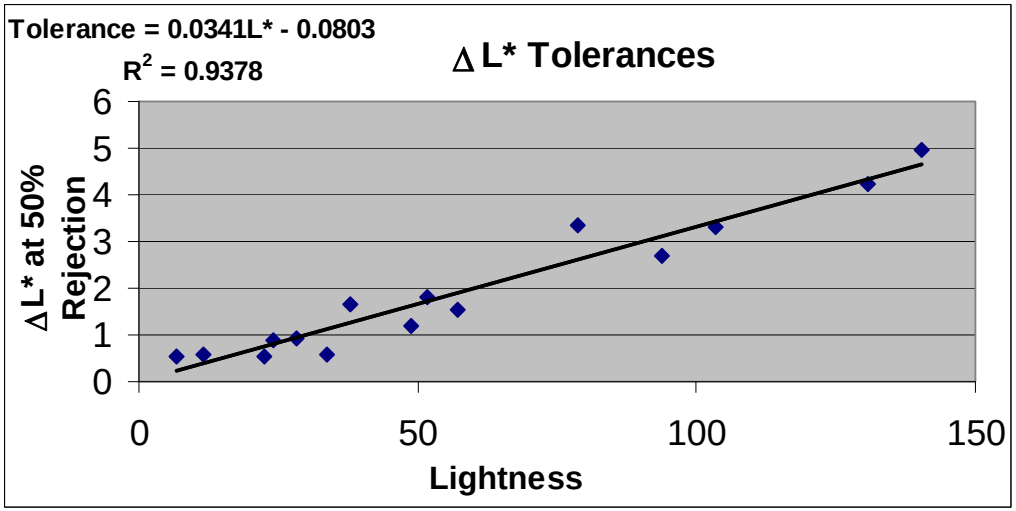
Results

Observed Tolerance ΔL* at 50% Rejection)

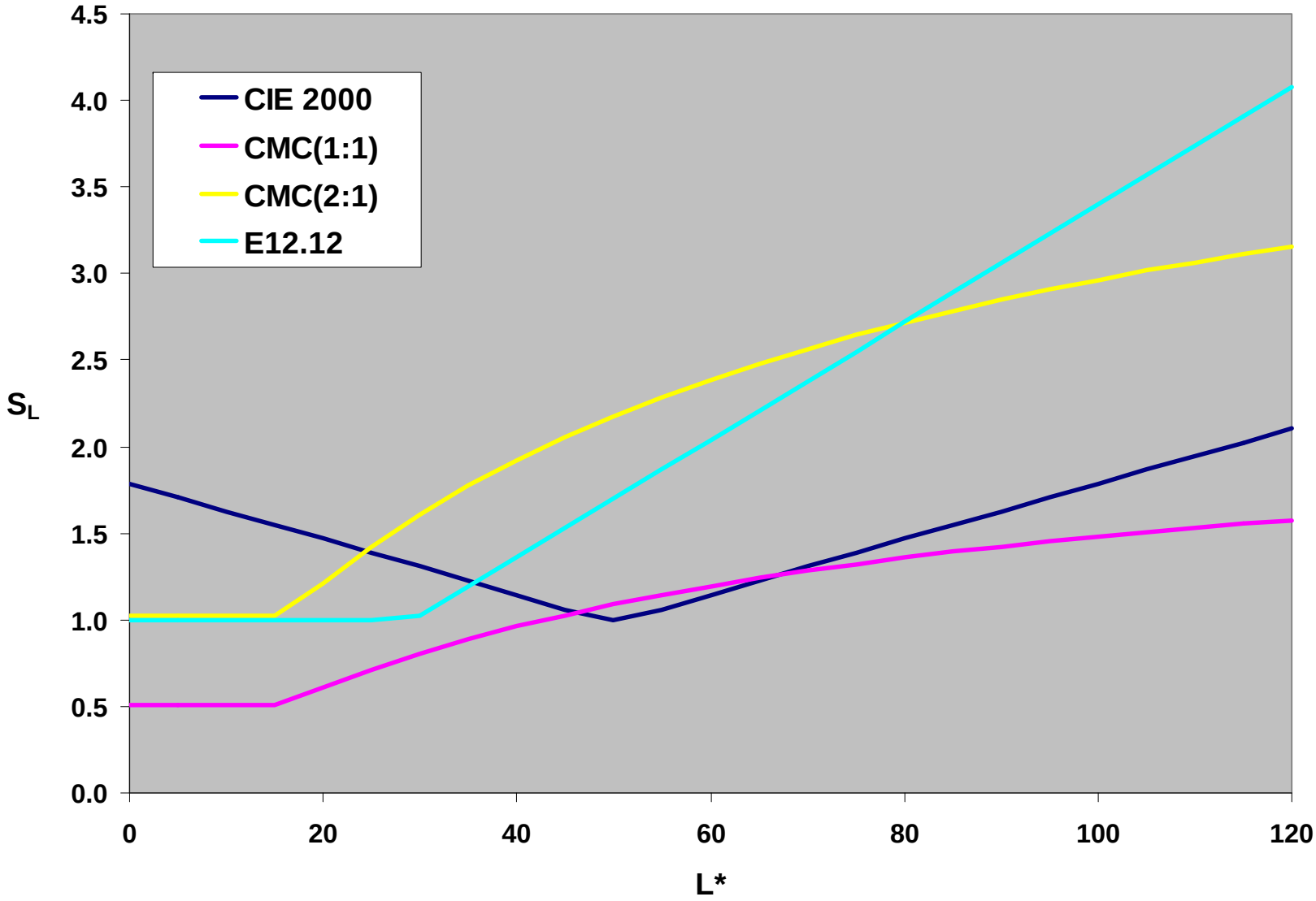
SERIES	15º	25º	45º	75º	110º
Light	4.98	3.29	1.53	1.67	0.57
Medium	4.25	2.71	1.20	0.92	0.52
Dark	3.36	1.81	0.88	0.59	0.52

Goodness of linear fit (R^2)

SERIES	15º	25º	45º	75º	110º
Light	0.76	0.96	0.82	0.73	0.76
Medium	0.81	0.92	0.83	0.98	0.98
Dark	0.74	0.79	0.84	0.99	0.99



S_L function comparison



S_L function in DIN 6175 = f(L*, aspecular angle)

dE Recommendation QC on an Assembly Line

Use CIE94 Equations

- Solid colors: $S_L = 1.0$
- Metallics:
  $S_L = 0.034L^*$ when $L^*>29.4$
  $S_L = 1.0$ when $L^*<29.4$

Set meaningful tolerances at **25°, 45°, 75°** based on history. These angles are not as sensitive to application.

Supplier tolerances at **15°, 45°, 110°** to ensure good match to standard.

May be added to ASTM D2244 as recommendation.

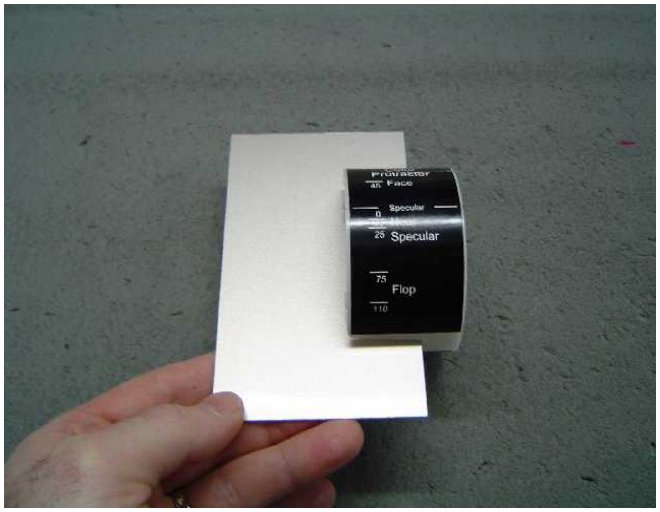
Future Standardization (cont.)
Viewing of Gonioapparent Materials

- When there are complaints about the measurement not matching the visual appraisal, it is often because the observer is not viewing the specimen at the proper geometry.
- ASTM E12.12 is forming a task group to explore standardization of viewing conditions.
- Here are some viewing aids currently available to help mitigate the problem.

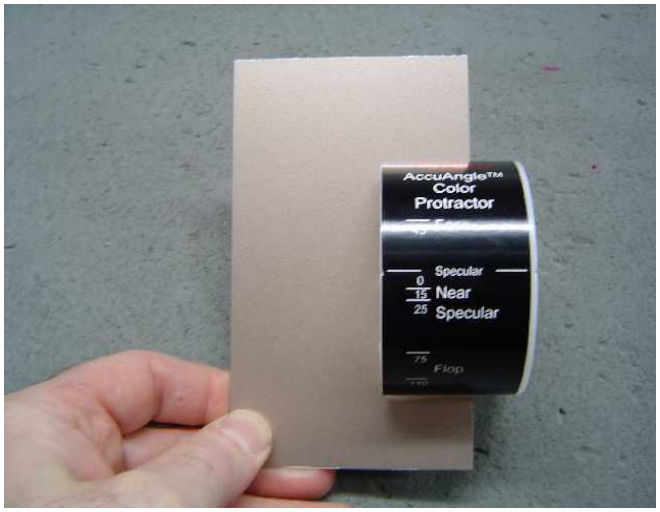
Panel Viewing Device I

DuPont AccuAngle™ Color Protractor

Near Aspecular 15°



Mid Aspecular 45°



Far Aspecular 110°

Note the light source reflected on the black background of the protractor used to define the aspecular angle.

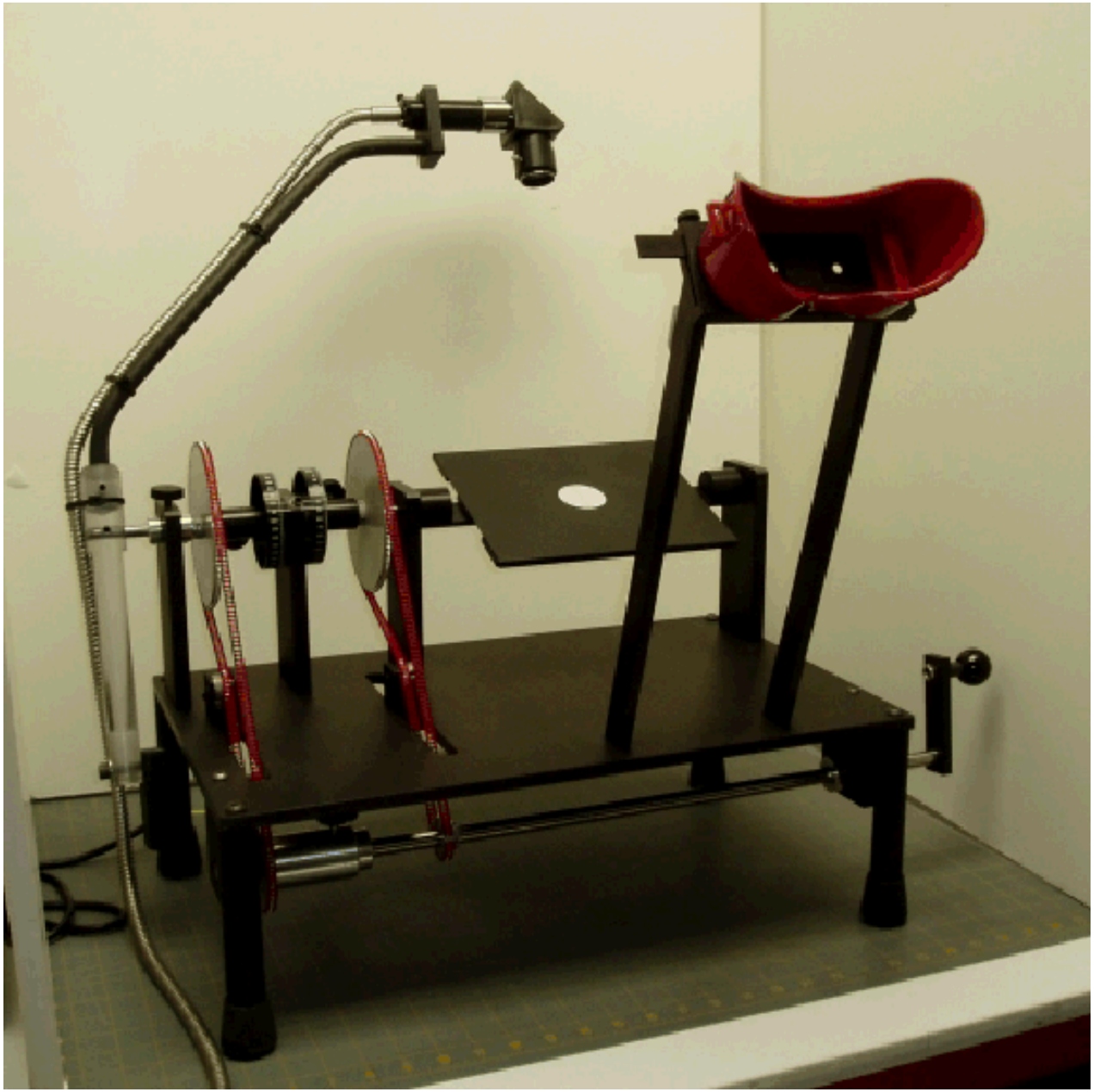
Panel Viewing Device II

Gonio-Vision-Box

Panel Viewing Device III

byko-spectra *effect*

Flex Products Viewer



Future Standardization (cont.)

Color difference and gonioapparent materials

- All existing dE equations are based on solid colored samples
- What is the best dE equation for this class of materials?

Visual evaluation

- New ASTM E12.12 Task group forming to study

New technologies F.Y.I.

New instruments for measurements of gonioapparent materials

(FYI only, technology has not been evaluated by E12.12)

19 different measurement angle combinations
Including a limited number of out-of-plane measurements
Includes all angle combinations specified in ASTM E2539

Graphics courtesy of: x-rite PANTONE

New instruments for measurements of gonioapparent materials

(FYI only, technology has not been evaluated by E12.12)

BYK-mac

6 different color measurement angle combinations
Sparkle characterization at 3 illumination angles
Graininess characterization under diffuse illumination

Graphics courtesy of: BYK Additives & Instruments

Where do we go from here?

A sales pitch for working with an established standard setting body…

Overview & Advantages of ASTM Standardization

- ASTM International . . . is a globally recognized leader in the development and delivery of **international voluntary consensus standards**. Today, some 12,000 ASTM standards are used around the world to improve product quality, enhance safety, facilitate market access and trade, and build consumer confidence.
- ASTM's leadership in international standards development is driven by the contributions of its members: more than 30,000 of the **world's top technical experts and business professionals** representing 135 countries. Working in an **open and transparent process** and using ASTM's advanced electronic infrastructure, ASTM members deliver the test methods, specifications, guides, and practices that support industries and governments worldwide.

The down side. . .

- Standards organizations tend to be slow
- Present economic realities have resulted in lower participation rate
- Companies need to protect proprietary technology slows progress

The plea. . .

- Resist the temptation to over specify, it adds cost and sets false expectations
- Tailor the specification to the application, the standards needs of pigment manufacturer are probably very different than those of a automobile company
- Active participation and cooperation is the key, together we can all win

My Thanks To:

- Allan Rodrigues (DuPont)
- Members of ASTM committee E-12.12
- Mike Nofi (Flex Products) for goniospectral measurements
- Dave Alman (DuPont) for metallics studies, early ANOVA analysis, and selected slides
- Jennifer VanMullekom (DuPont) for statistics assistance
- X-Rite, BYK, and Merck for contribution of selected graphics