Correlation Between Solids Content and Hiding as it Relates to Calculation of VOC Content in Architectural Coatings

Albert C. Censullo

Dane R. Jones

Max T. Wills

Department of Chemistry and Biochemistry

Cal Poly State University

San Luis Obispo, CA

CAL POLY

Background

- Architectural Coatings are a significant source of VOC emissions in California
- about 46 tons/day from water-borne coatings
- about 64 tons/day from solvent-borne coatings

Source: 2001 ARB Architectural Coatings Survey

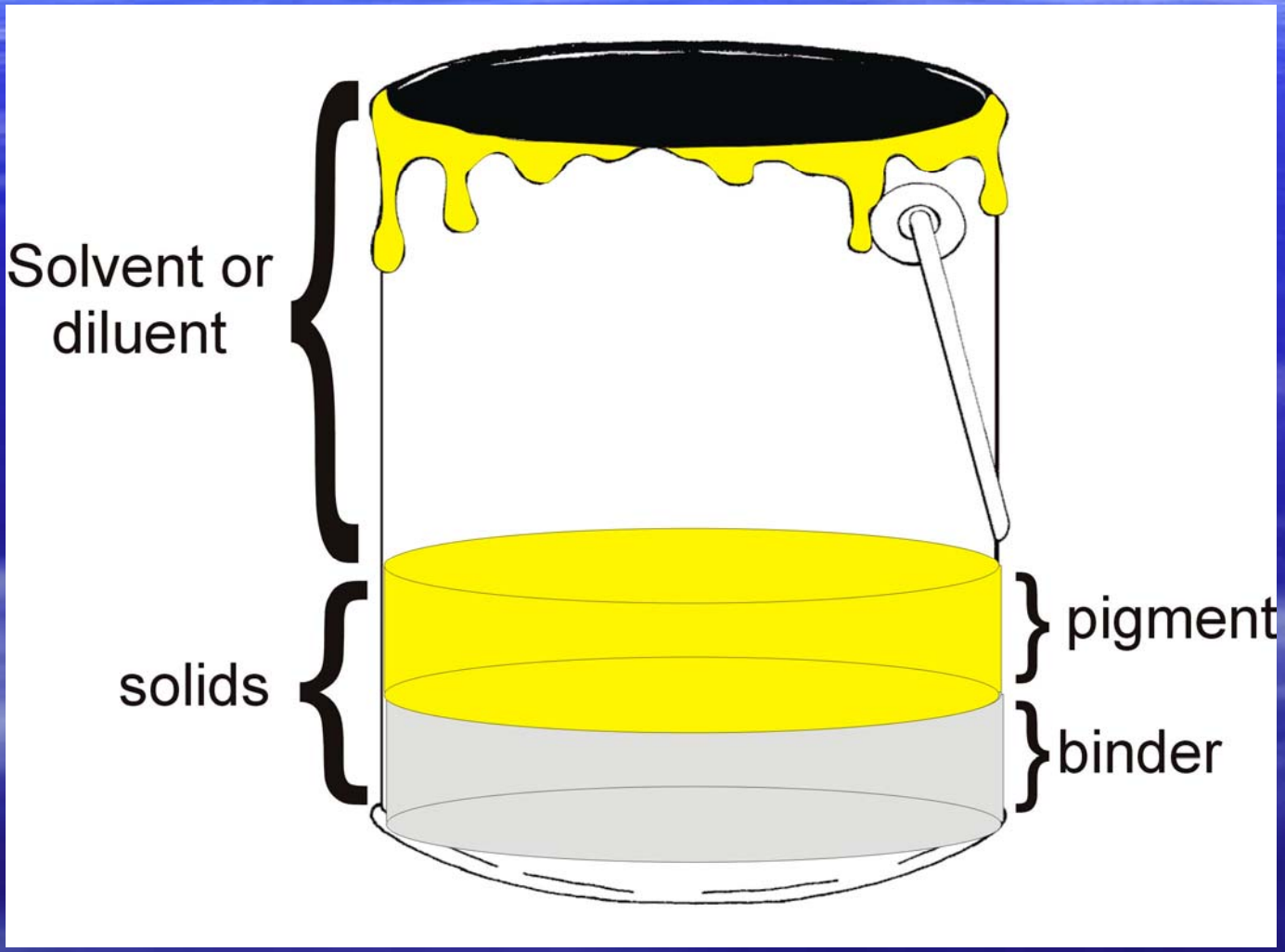
Regulation of VOCs in Coatings

- End result of applying coating is to deposit solids on a substrate
- Regulators concerned with amount of VOC emissions per volume of coating solids deposited
- When VOC regulations were originally developed, no acceptable, recognized standard method for determining the volume of coating solids was available
- To describe the VOC content of coatings, EPA settled on a measure known as “regulatory VOC”

Coating VOC Definitions

- Actual VOC (or material VOC)
  - grams of VOC per unit volume of liquid coating
- Regulatory VOC (or coating VOC)
  - For solvent borne coatings, grams of VOC per volume of coating minus the volume of exempt solvents (if any)
  - For water borne coatings, grams of VOC per volume of coating minus the volume of water minus the volume of exempt solvents (if any)

Coating Composition



Coating VOC Definitions

Solvent-borne coatings

$$actual\ VOC = \frac{g\ VOC}{L_{solids} + L_{VOC}}$$

$$L_{coating} = L_{solids} + L_{VOC}$$

$$regulatory\ VOC = \frac{g\ VOC}{L_{solids} + L_{VOC}} \quad or$$

$$regulatory\ VOC = \frac{g\ VOC}{L_{coating}}$$

water-borne coatings

$$actual\ VOC = \frac{g\ VOC}{L_{solids} + L_{VOC} + L_{water}}$$

$$L_{coating} = L_{solids} + L_{VOC} + L_{water}$$

$$L_{coating} - L_{water} = L_{solids} + L_{VOC}$$

$$regulatory\ VOC = \frac{g\ VOC}{L_{solids} + L_{VOC}} \quad or$$

$$regulatory\ VOC = \frac{g\ VOC}{L_{coating} - L_{water}}$$

Effect of Solids Volume on Regulatory VOC

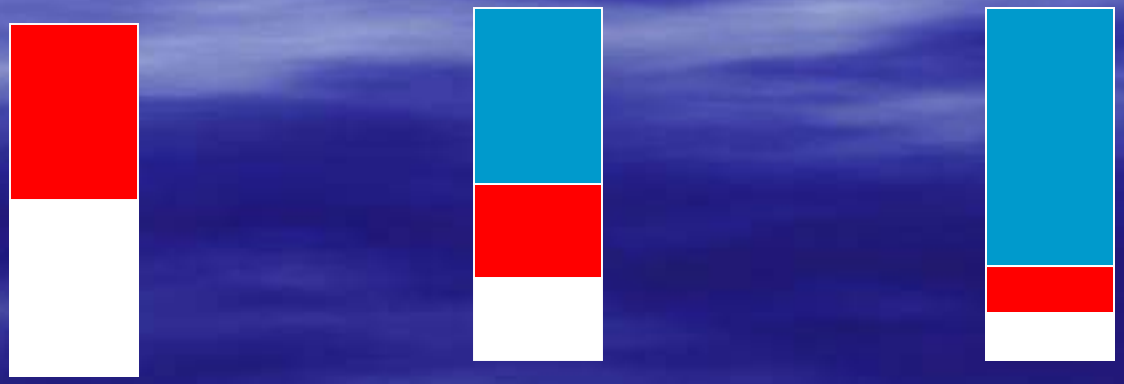
Hypothetical Solvent-based Coatings

Paint	Solids Volume(Liters)	VOC Volume (Liters)	Water Volume (Liters)	Regulatory VOC, g/L-water	Solids Volume per Liter of Liquid Paint	VOC content g per Liter of Paint Solids
1	0.75	0.25	0	250	0.75	333
2	0.625	0.375	0	375	0.625	600
3	0.5	0.5	0	500	0.5	1000
4	0.375	0.625	0	625	0.375	1667
5	0.25	0.75	0	750	0.25	3000
6	0.125	0.875	0	875	0.125	7000

Effect of Solids Volume on Regulatory VOC

Hypothetical Water-based Coatings

Paint	Solids Volume (Liters)	VOC Volume(Liters)	Water Volume(Liters)	Regulatory VOC, g/L-water	Solids Volume per Liter of Liquid Paint	VOC content, g per Liter of Paint Solids
7	0.5	0.5	0	500	0.5	1000
8	0.375	0.375	0.25	500	0.375	1000
9	0.25	0.25	0.5	500	0.25	1000
10	0.125	0.125	0.75	500	0.125	1000



HIDING vs. COVERAGE

Hiding VOC

- Proposed “figure of merit”
- definition: grams VOC emitted per unit area (1.00 m^2) of a hiding film (having a contrast ratio of 0.98)
- Performance-based measure
- In equation form,

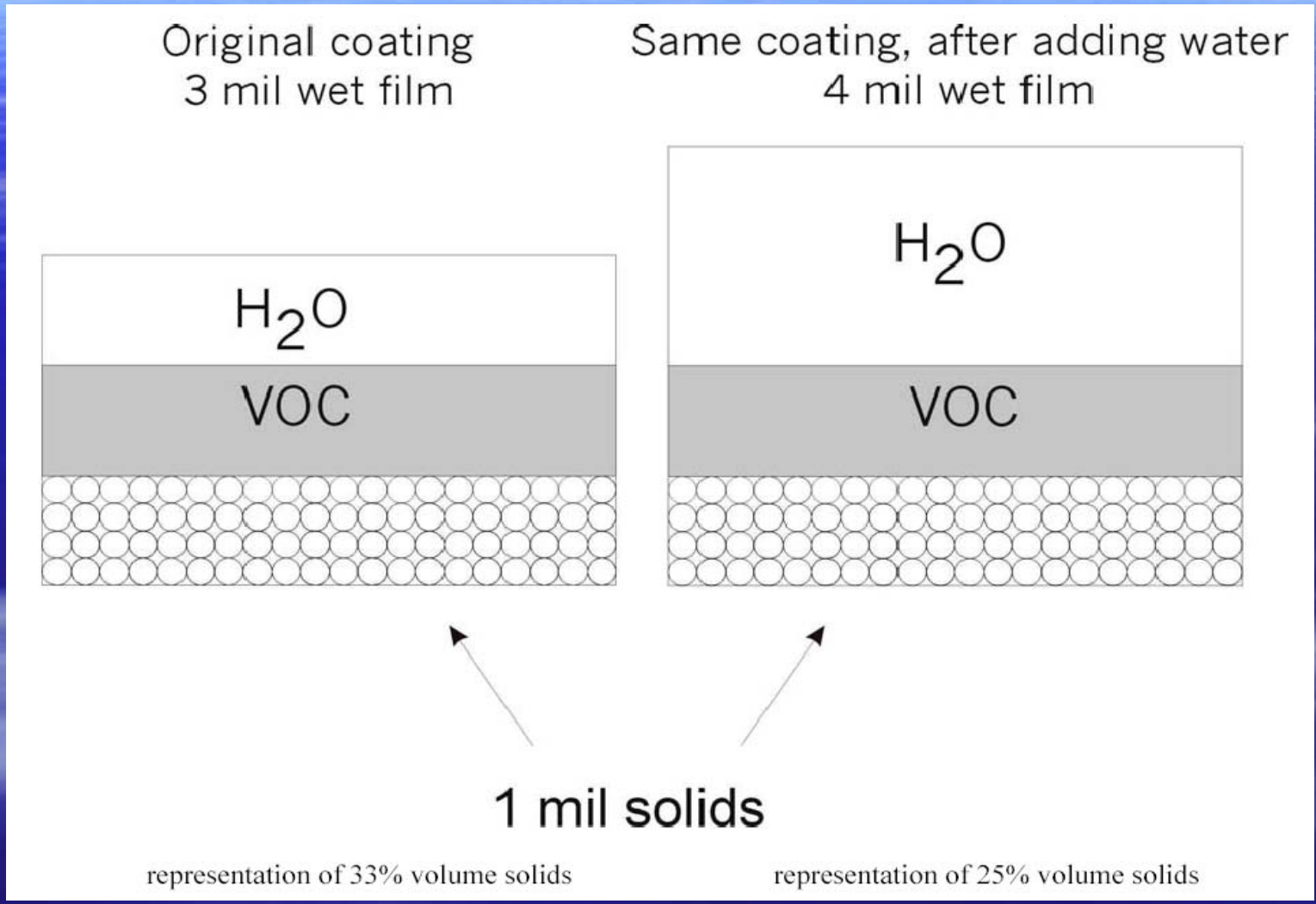
$$hiding\ VOC = \frac{actual\ VOC}{H_{0.98}}$$

where $H_{0.98}$ is the hiding power, per ASTM D2805

Hiding VOC and Coating "families"

- Hiding is a characteristic of the dried film
- Hiding ability depends on nature and quantity of pigments, binders and extenders
- Hiding power measurements at *one* film thickness can be used to calculate hiding at *any* film thickness
- A family of coatings may be prepared having identical solids composition, and variable percent solids

Example of a Coating "family"



Project Goals

- Investigate relationship between total volume solids content, coverage, hiding, and VOC for common classes of architectural coatings
- Determine “effective” or “hiding” VOC content of architectural coatings
- Formulate and test 20 water-based and 10 solvent-based coatings

Hiding Power

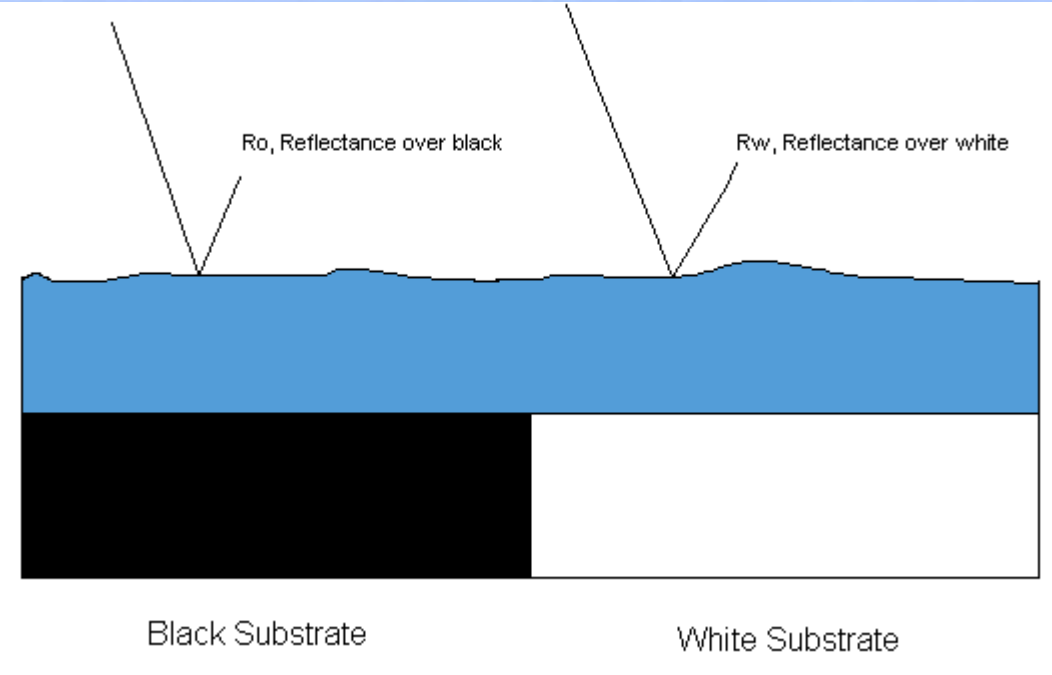
- Hiding Power is defined as the spreading rate, in m^2/L required for *full hiding* of the substrate
- A coating is considered to have *full hiding* when its dry film produces a contrast ratio, C_w of 0.98
- C_w is the ratio of the reflectance of a black substrate to the reflectance of a white substrate, $C_w = R_o/R_w$
- Ref: ASTM D 2805-96a

Measuring Hiding Power

ASTM D2805-96a Definitions

- R_o reflectance of film on black surface
- R_w reflectance of film on white surface of reflectance W
- W reflectance of white substrate
- R_{inf} reflectivity of a film having the same reflectance over black and white substrates
- A film area, cm^2
- N non-volatile content of paint, expressed as a mass fraction
- D paint density, g/mL
- M weight of film, in grams
- H_x Spread rate, m^2/L
- S scattering coefficient
- $H_{0.98}$ hiding power, m^2/L, the spreading rate producing a contrast ratio of 0.98

Measuring Hiding Power



R_∞ is reflectance at thickness where $R_o = R_w$

H_x is the experimental spread rate, in m^2/L

H_x = (film area cm^2) x (NVM) x (density g/mL)/10 M

NVM = non-volatiles by mass

Measuring Hiding Power

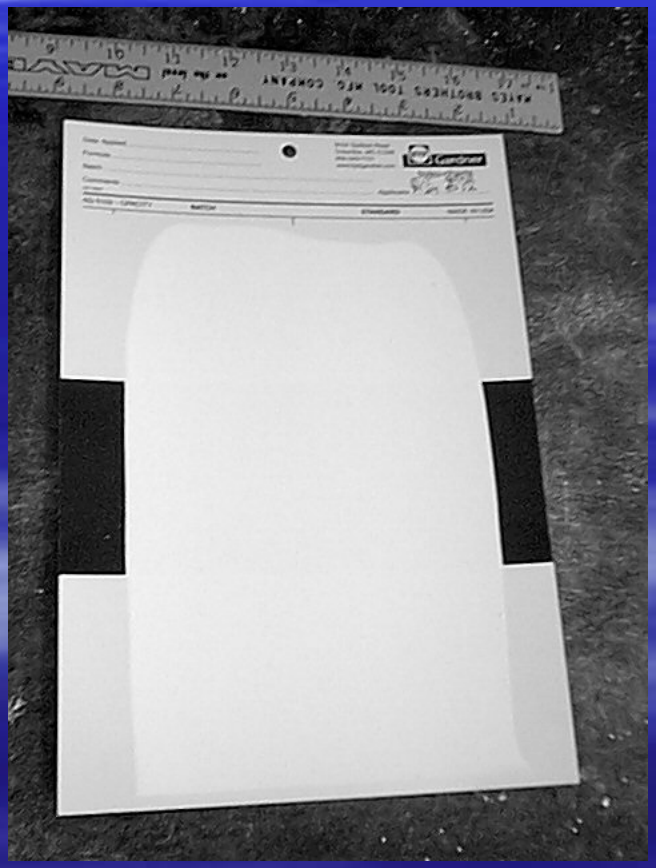
- Equations used to calculate hiding power based on the Kubelka-Munk turbid media theory
- Reflectance values for films for each film are measured
- The reflectance values then used to calculate R_∞
- The spread rate H_x, in m^2/L for the coating on black glass is measured
- The scattering coefficient, S, can then be calculated using R_∞ , and R_o and H_x from a film on black glass
- The scattering coefficient and R_∞ used to calculate the hiding power for 0.98 contrast ratio, or $H_{0.98}$ in m^2/L

Hiding Power Determination

- ASTM D 2805-96a, the standard test method for measuring the hiding power of a coating through reflectometry.
- BYK-Gardener™ AG-5102 Opacity Charts
- Leneta GB-2a Blacklite™ Black Carrara Glass
- Datacolor Mercury Spectrometer

Hiding Power Determination

Drawdown on Coated Paper Chart



Hiding Power Determination

Drawdown on Black Glass

Coating Formulations

- The coatings were prepared in accordance with standard industrial practices.
- Dry pigments were combined with dispersants and other additives under high shear using a high speed disperser to produce a pigment grind.
- The fineness of the grind was then tested using a grind gauge.
- Resin and the remaining ingredients were then added during the letdown stage under low shear agitation.

Coating Analysis and Application

- ASTM D 3924-80, establishing a standard for the environment under which coatings are conditioned and tested
- ASTM D 823-95 Practice E, the standard for producing coating films of uniform thickness using a hand held blade
- ASTM D 1475-98, the procedure for measuring the density of a coating
- VOC (Volatile Organic Compounds), Method 24
- NVM (non-volatiles by mass), per ASTM D2805-96a

Theoretical Hiding Power Determination for Given Coating

- Assumptions
  - Dry films for each coating within a given family are identical
  - Reflectance values, R_w, W, R_∞, and R_o, all depend on the nature of the film from which the readings were taken
  - The speeds at which the films are drawn is identical
  - The environment in which the films are cured is identical
  - Coating contents only vary in the relative amount of water present in each coating

Water-based Coatings Investigated

#	type	VOC* (reg)	VOC* (actual)	NVV	PVC	Resin	Extenders
1	flat	100	36	34	42	vinyl acrylic EPS 2911	$CaCO_3$, clay
2	flat	100	36	34	42	vinyl acrylic EPS 2911	neph.syn., clay
3	flat	105	39	33	40	vinyl acrylic EPS 2911	$CaCO_3$, clay, opaque polymer
4	flat	7.9	3	35	42	VAE Duravace FT-320	$CaCO_3$, clay
5	flat	8.1	3	34	42	VAE Duravace FT-320	neph.syn., clay
6	flat	7.8	3	34	42	VAE Duravace FT-320	$CaCO_3$, clay, opaque polymer
7	eggshell	14	5	33	38	vinyl acrylic Rovace 9900	clay
8	eggshell	80	29	33	33	vinyl acrylic Rovace 9900	clay, opaque polymer
9	eggshell	104	36	33	33	vinyl acrylic EPS 2911	neph.syn., clay
10	eggshell	8.2	3	33	33	VAE Duravace FT-320	clay

Water-based Coatings Investigated

#	type	VOC* (reg)	VOC* (actual)	NVV	PVC	Resin	Extenders
11	eggshell	8.8	3	34	33	VAE Duravace FT-320	clay, opaque polymer
12	eggshell	8.4	3	33	33	VAE Duravace FT-320	neph.syn., clay
13	semigloss	112	41	33	26	vinyl acrylic EPS 2911	none
14	semigloss	117	44	33	26	vinyl acrylic EPS 2911	opaque polymer
15	semigloss	68	25	33	25	100% acrylic Rhoplex SG-10M	none
16	semigloss	68	25	33	25	100% acrylic Rhoplex SG-10M	opaque polymer
17	semigloss	7.2	2	34	25	100% acrylic Rhoplex SG-10M	none
18	semigloss	225	96	32	26	100% acrylic Rhoplex SG-10M	opaque polymer
19	gloss	0	0	33	20	100% acrylic low VOC Rhoplex SF-012	none
20	gloss	156	62	33	20	100% acrylic Rhoplex HG-700	none

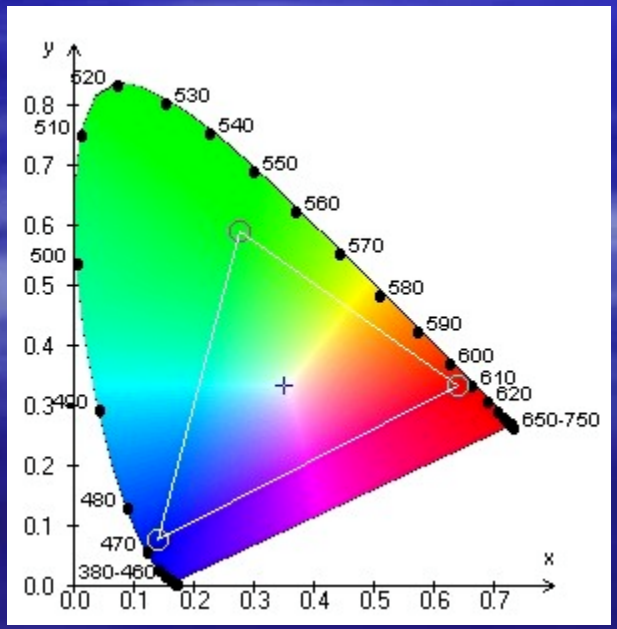
Solvent-based Coatings Investigated

#	type	VOC* (reg)	VOC* (actual)	NVV	PVC	Resin	Extenders
21	flat	364	364	56	58	long oil soya alkyd EPS 6604	neph.syn., $CaCO_3$
22	flat	370	370	55	60	long oil soya alkyd EPS 6604	clay, $CaCO_3$
23	eggshell	344	344	61	50	long oil soya alkyd EPS 6604	neph.syn., $CaCO_3$
24	eggshell	331	331	58	50	long oil soya alkyd EPS 6604	clay, $CaCO_3$
25	eggshell	247	247	70	49	long oil soya alkyd, low VOC EPS 6611	neph.syn., $CaCO_3$
26	semigloss	331	331	60	40	long oil tofa alkyd Beckosol 10-029	none
27	semigloss	365	365	55	35	long oil soya alkyd EPS 6604	none
28	semigloss	200	200	77	37	long oil soya alkyd, low VOC EPS 6611	none
29	gloss	317	317	59	13	long oil soya alkyd EPS 6604 Dextrol OC70	none
30	gloss	207	207	73	10	long oil soya alkyd, low VOC EPS 6611 EPS 6604	none

Color Determinations

CIE XYZ system

- X primary receptor sensitive to red-orange
- Y primary receptor sensitive to green
- Z primary receptor sensitive to blue
- A given color may be represented by a set of (X,Y,Z) coordinates in color space

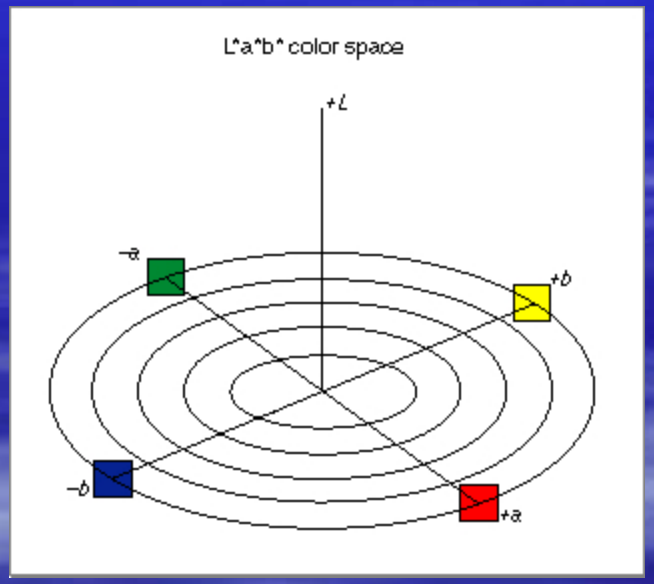


Color Determinations

CIE L*a*b* system

Transformation of XYZ system into “Synthetic Primaries”

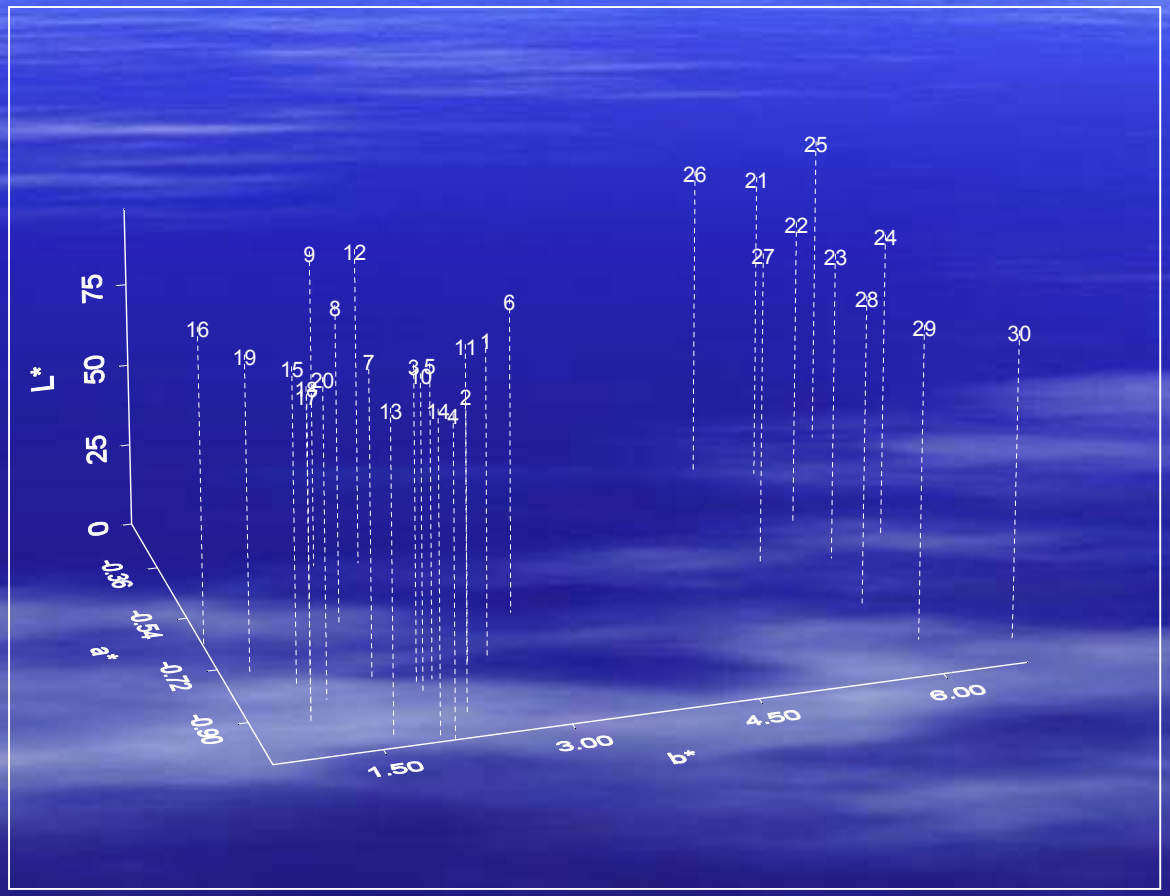
- L* luminance (brightness)
  - Range: 0 to 100
- a* red-green color axis
  - Negative values increasing green
  - Positive values increasing red
- b* blue-yellow color axis
  - Negative values increasing blue
  - Positive values increasing yellow
- ΔE color difference



$$\Delta E = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 (\Delta L^*)^2}$$

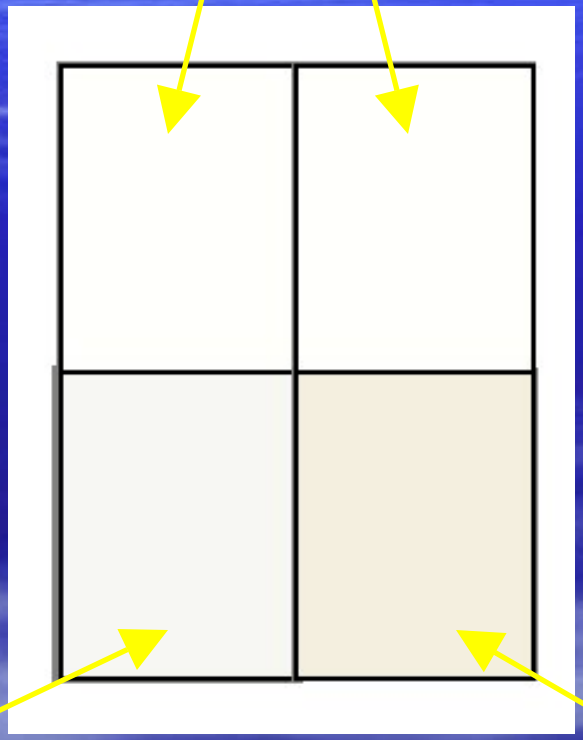
Color Determinations

A Portion of L*a*b* Color Space for Coatings



ARB numbers 21-30 are solvent-based coatings

Color Determinations



Hiding VOC
Water-Based Coatings

#	type	VOC*(reg)	VOC* (actual)	$H_{0.98}$ (m^2/L)	VOC $H_{0.98}$ (g/m^2)
1	flat	100	36	6.4	5.6
2	flat	100	36	6.7	5.4
3	flat	105	39	5.1	7.6
4	flat	7.9	3	5.7	0.5
5	flat	8.1	3	6.7	0.4
6	flat	7.8	3	6.3	0.5
7	eggshell	14	5	6.6	0.8
8	eggshell	80	29	7.3	4.0
9	eggshell	104	36	6.4	5.6
10	eggshell	8.2	3	5.4	0.6

Hiding VOC
Water-Based Coatings

#	type	VOC*(reg)	VOC* (actual)	$H_{0.98}$ (m^2/L)	VOC $H_{0.98}$ (g/m^2)
11	eggshell	8.8	3	6.9	0.4
12	eggshell	8.4	3	6.4	0.5
13	semigloss	112	41	8	5.1
14	semigloss	117	44	6.9	6.4
15	semigloss	68	25	6.5	3.8
16	semigloss	68	25	6.8	3.7
17	semigloss	7.2	2	7.3	0.3
18	semigloss	225	96	6.2	15.5
19	gloss	0	0	7.2	0
20	gloss	156	62	7.2	8.6

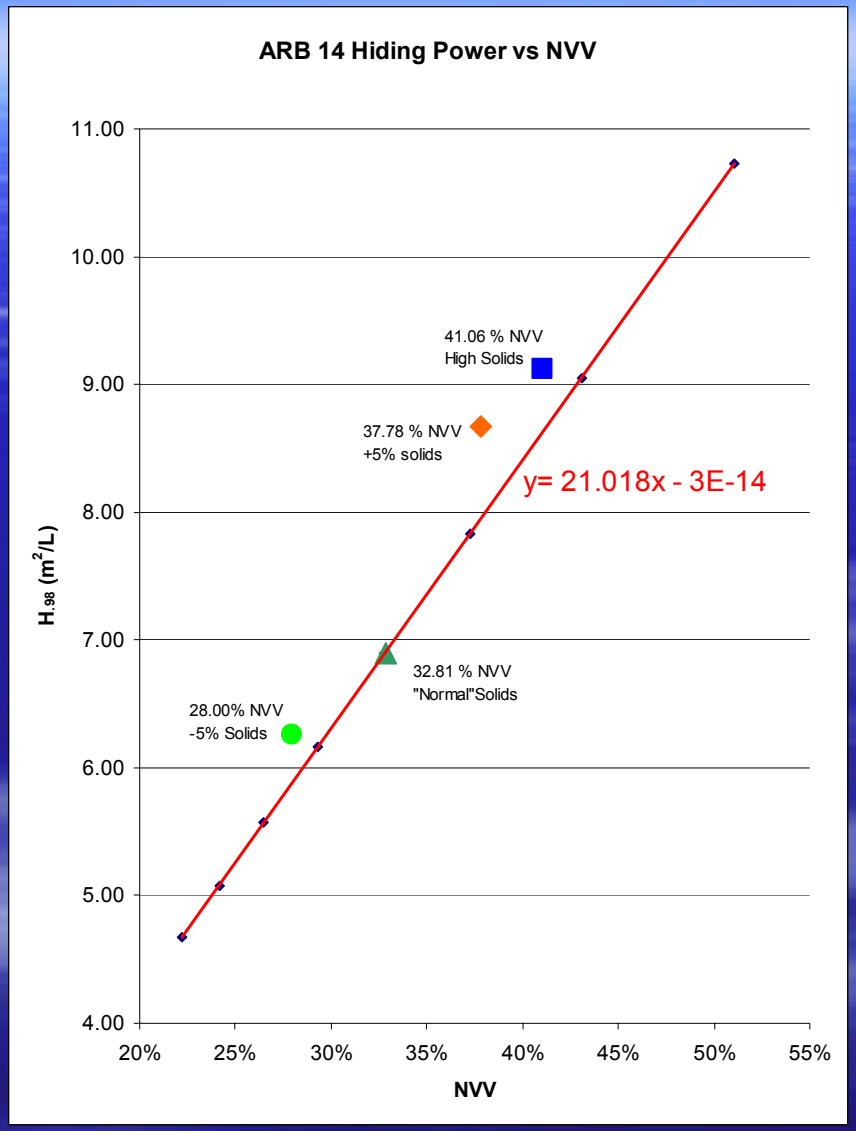
Solvent-based Coatings

Paint	Type	VOC (g/L)	Avg $H_{0.98}$ (m^2/L)	$H_{0.98}$ VOC (g/m^2)
21	Flat	360	5.64	65
22	Flat	370	8.40	44
23	Eggshell	344	6.52	53
24	Eggshell	331	8.55	39
25	Eggshell	247	6.67	37
26	Semigloss	331	7.54	44
27	Semigloss	365	9.06	40
28	Semigloss	200	8.81	23
29	Gloss	317	8.90	36
30	Gloss	207	9.10	23

Predictive Ability of Hiding Power

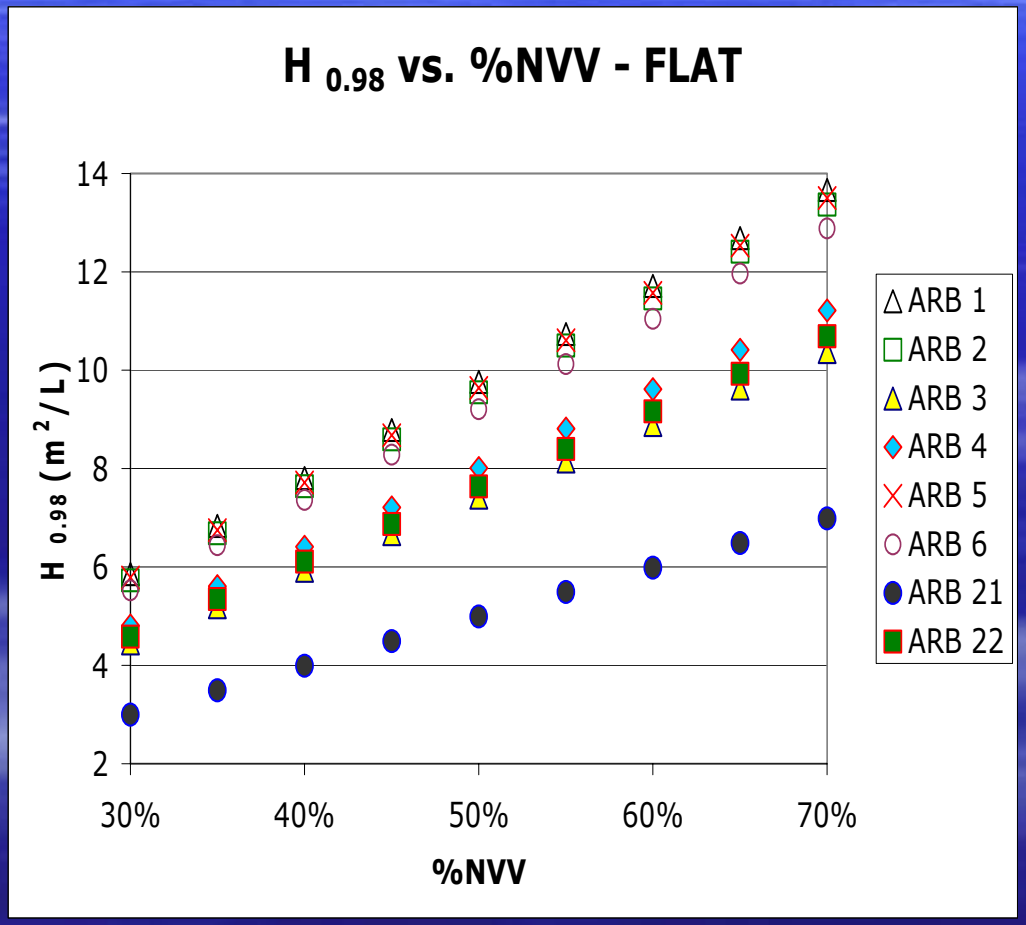
- Kubelka-Munk equations were used to predict hiding power for members of a given coating family
- For each family, a “parent” coating was characterized
- Other members of the family were differentiated only by %NVV
- A graph of Hiding Power vs. %NVV was prepared for each coating family

Predictive Ability of Hiding Power



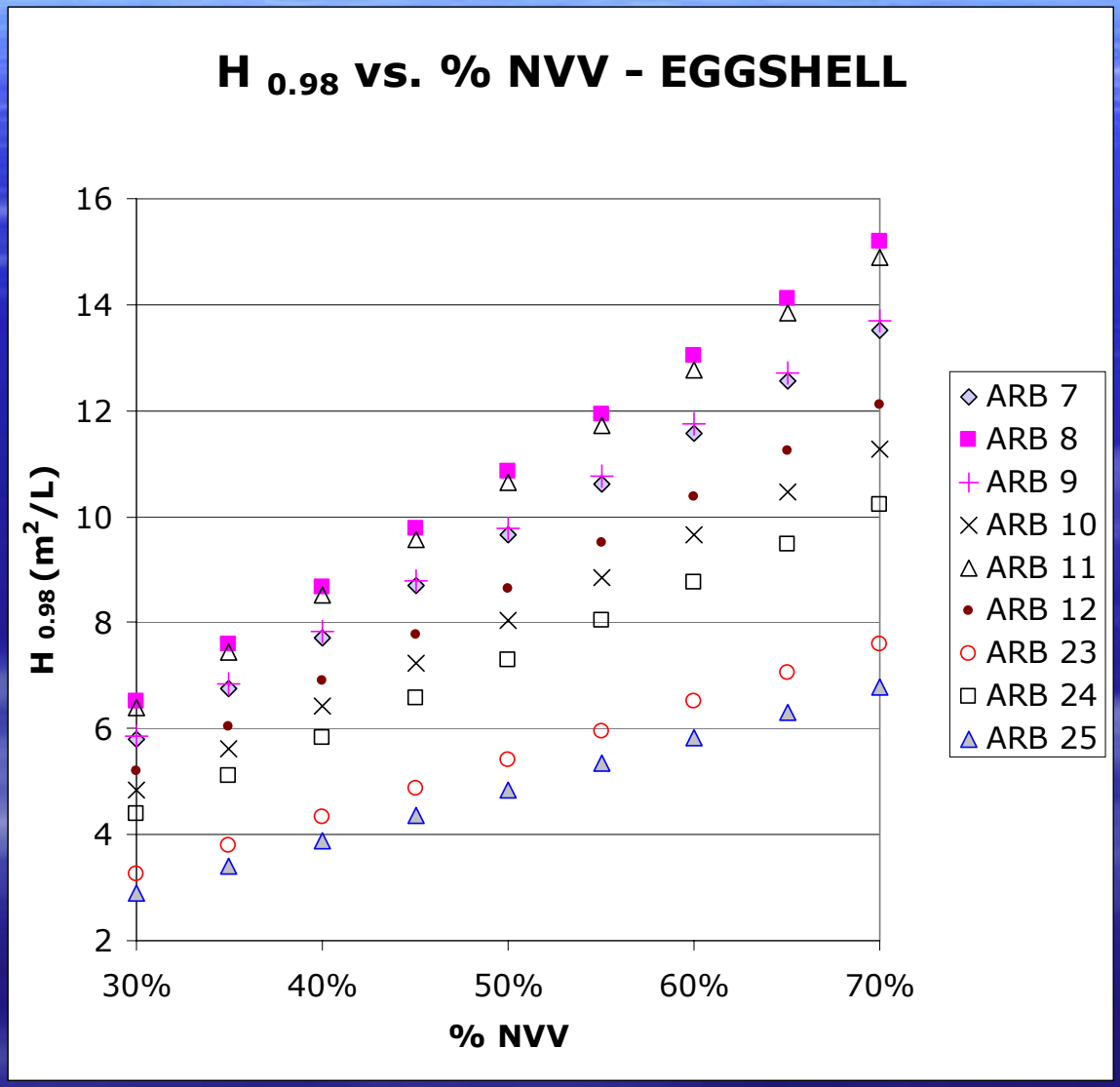
Results

Predicted Hiding Power for Flats



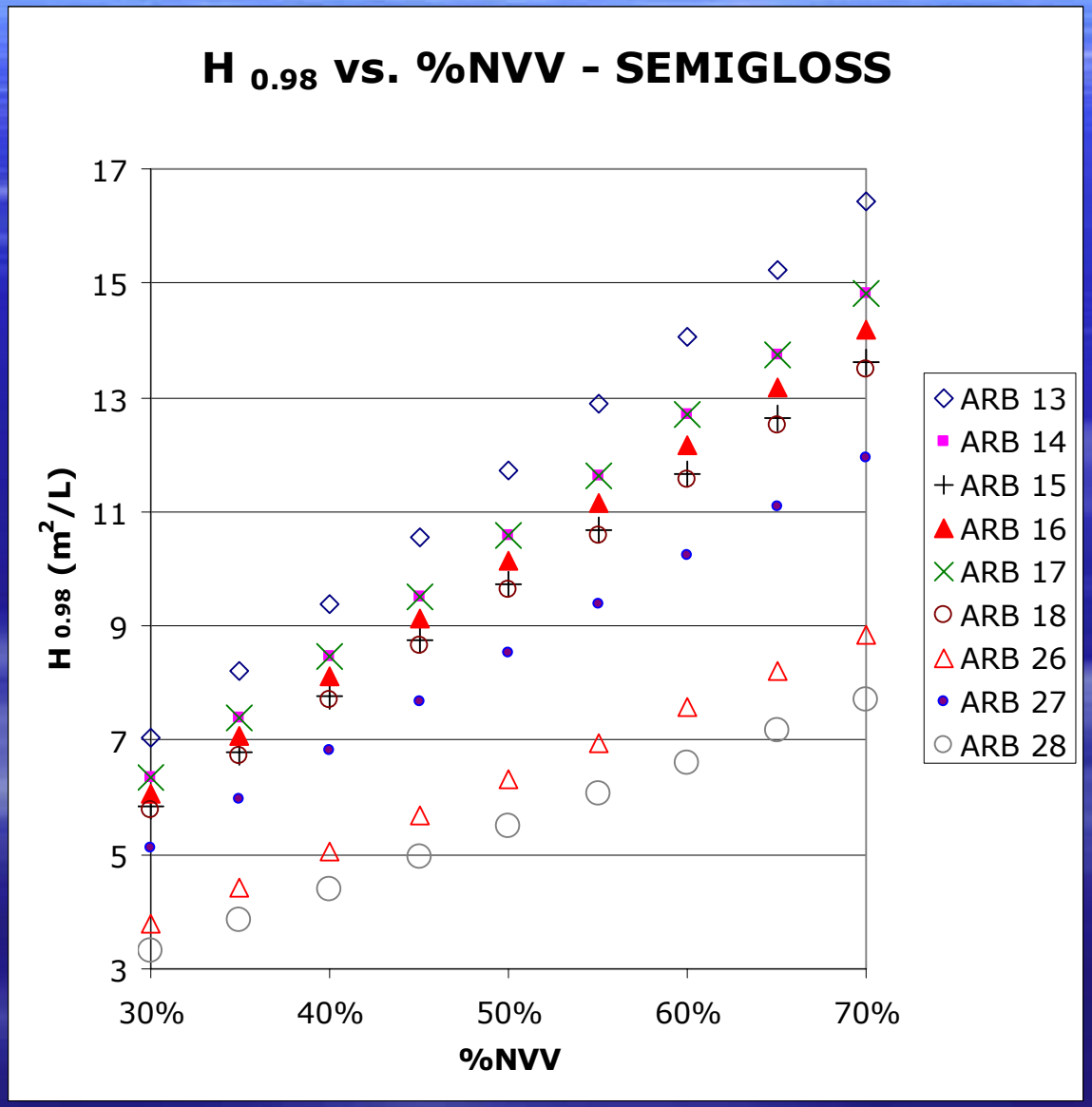
Results

Predicted Hiding Power for Eggshell



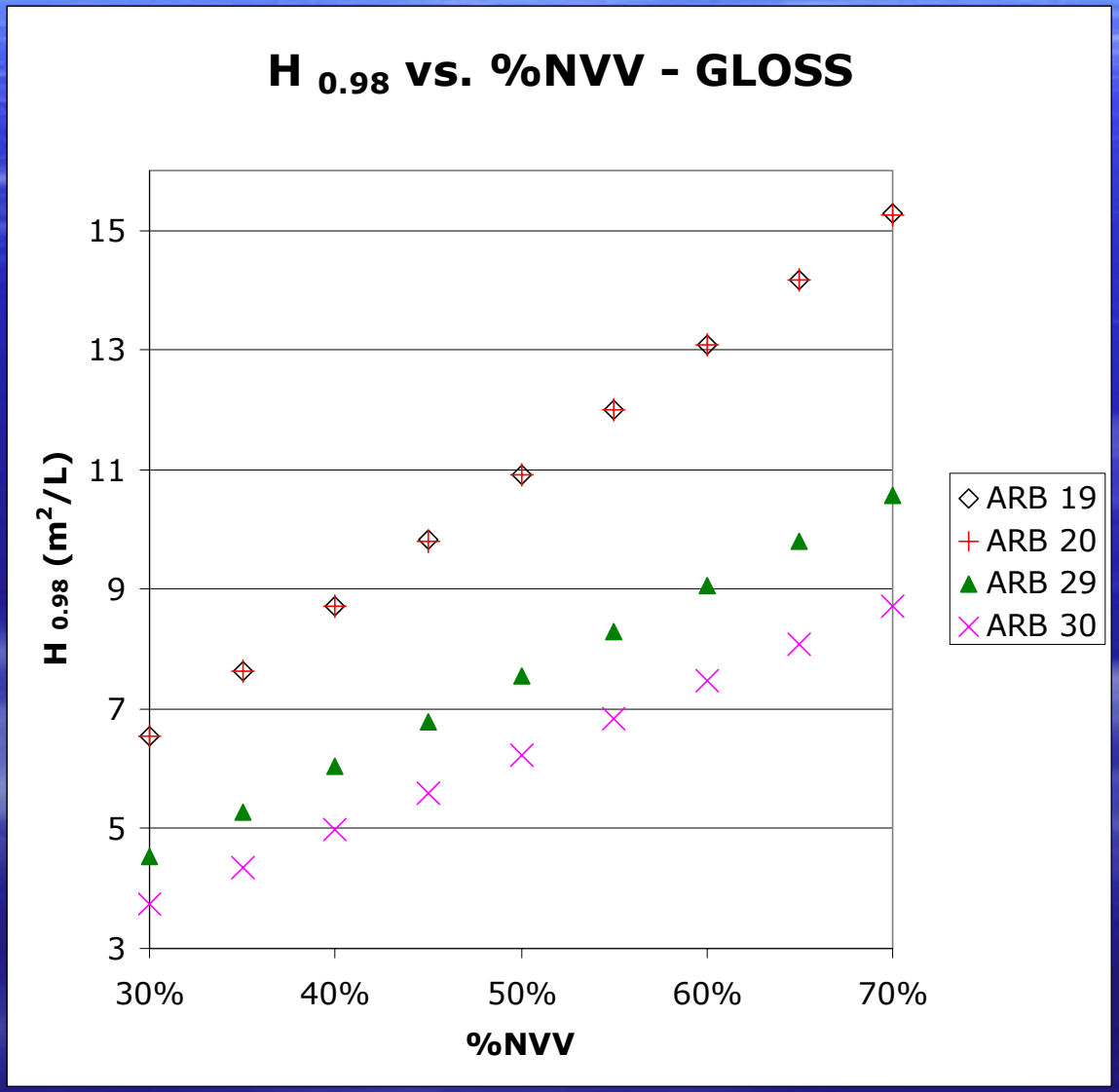
Results

Predicted Hiding Power for Semigloss

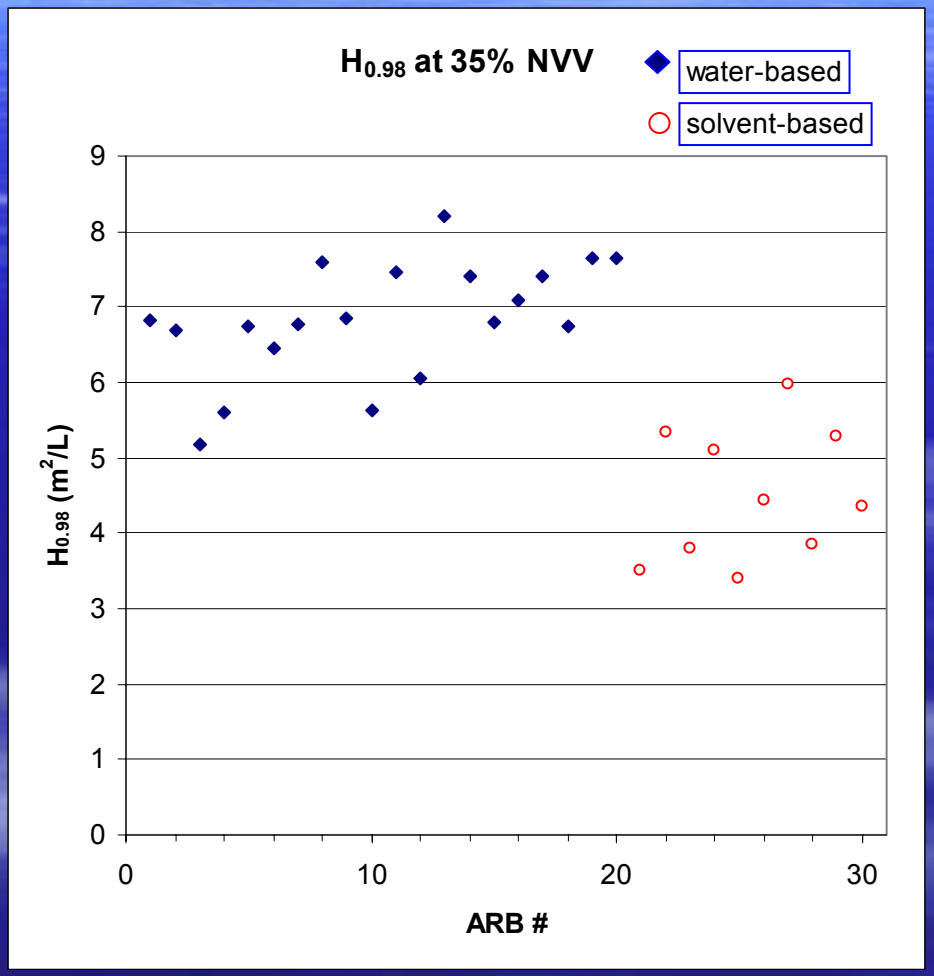


Results

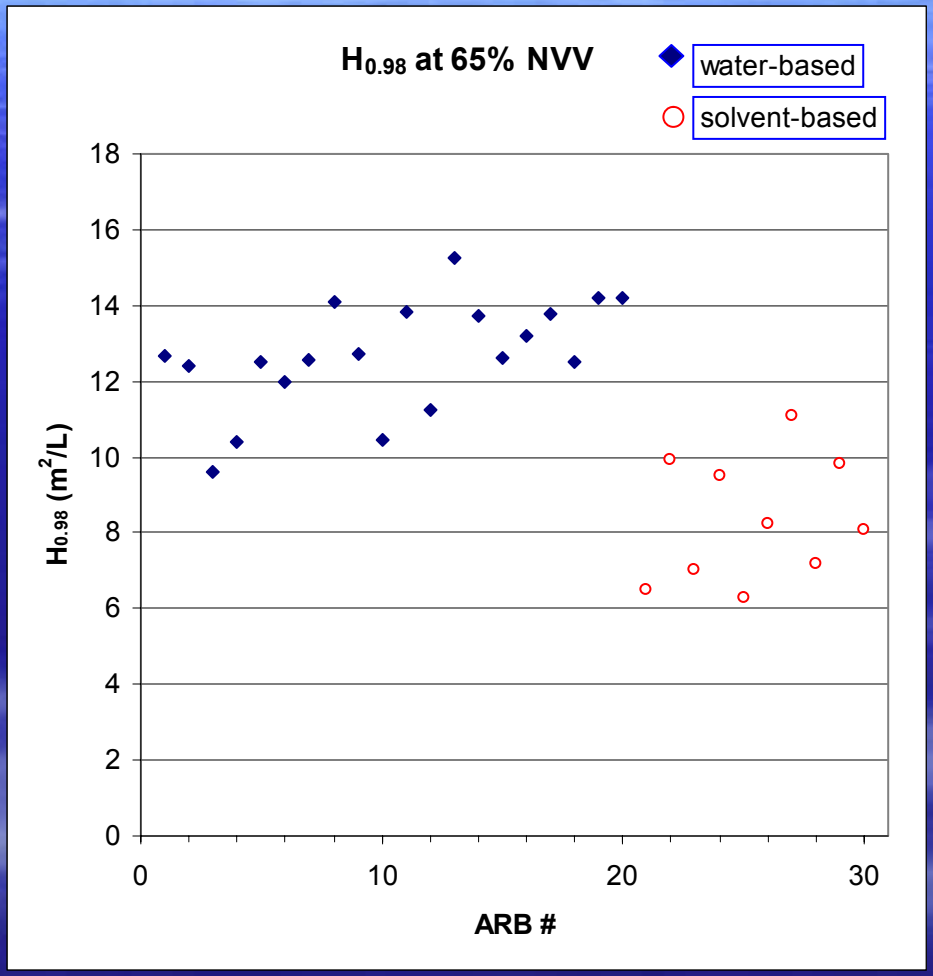
Predicted Hiding Power for Gloss



Predicted Hiding Power for all Coatings Normalized to 35% solids



Predicted Hiding Power for all Coatings Normalized to 65% solids



VOC Emissions from Coatings

- VOCs are released during application
- Amount of emitted VOC depends on two independent factors
  - VOC content of coating (g VOC/$L_{coating}$)
  - Volume of coating used

g VOC emitted = VOC_{actual} x $L_{coating}$ used

VOC Emissions from Coatings

- Consider a “test room”, 10’ x 12’, 8’ ceiling
- Wall area = 352 ft^2 = 32.7 m^2
- Assume consumer will apply coating until substrate is hidden
- From hiding power, $H_{0.98}$, calculate # liters to hide 32.7 m^2
  - Liters = Area/$H_{0.98}$
- From VOC_{actual} , calculate grams VOC emitted
  - g VOC emitted = VOC_{actual} x $L_{coating}$ used

VOC Emissions from Coatings

				VOC Measures					
#	type	solvent	%NVV	$H_{0.98}$ m^2/L	VOC_{reg} g/L	VOC_{actual} g/L	VOC $H_{0.98}$ g/m^2	liters to hide 32.7 m^2	VOC emitted (g)
1	flat	water	34	6.4	100	36	5.6	5.14	**185**
2	flat	water	34	6.7	100	36	5.4	4.91	**177**
3	flat	water	33	5.1	105	39	7.6	6.45	**252**
4	flat	water	35	5.7	7.9	3	0.5	5.77	**17**
5	flat	water	34	6.7	8.1	3	0.4	4.91	**15**
6	flat	water	34	6.3	7.8	3	0.5	5.22	**16**
7	eggshell	water	33	6.6	14	5	0.8	4.98	**25**
8	eggshell	water	33	7.3	80	29	4.0	4.51	**131**
9	eggshell	water	33	6.4	104	36	5.6	5.14	**185**
10	eggshell	water	33	5.4	8.2	3	0.6	6.09	**18**

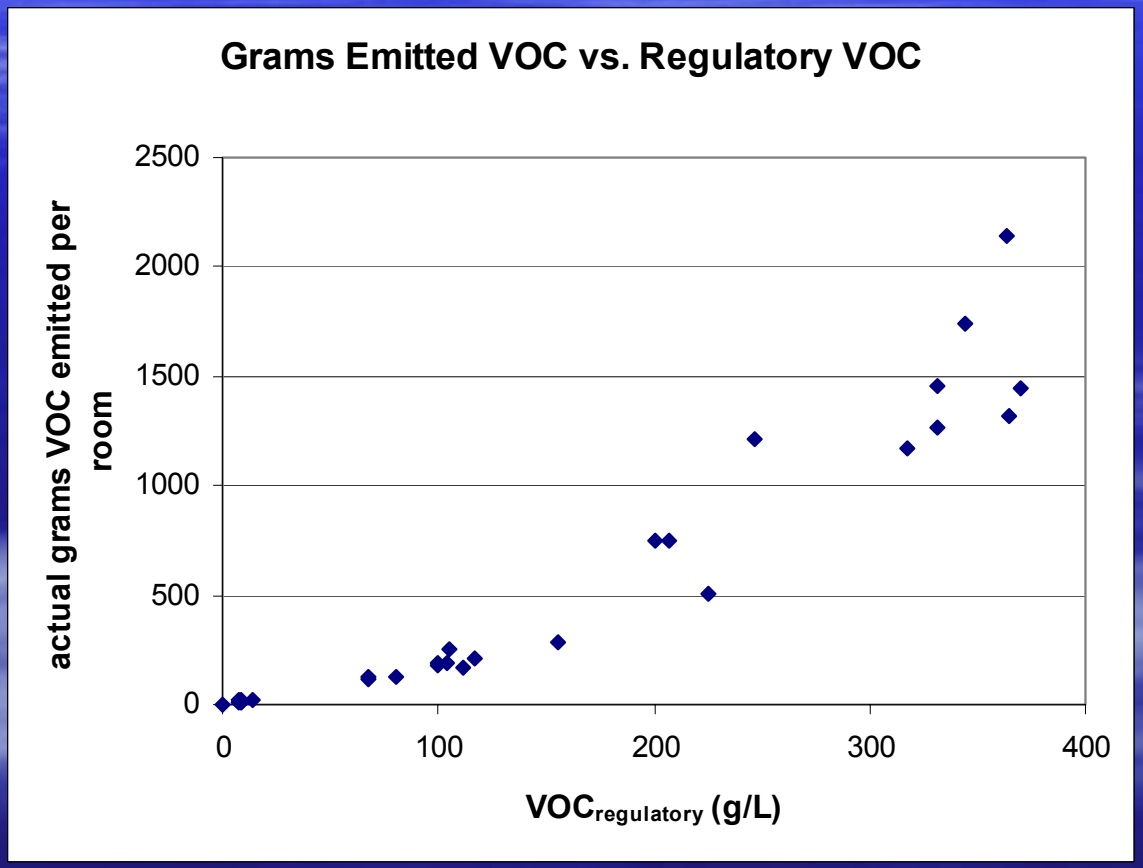
VOC Emissions from Coatings

					VOC Measures				
#	type	solvent	%NVV	$H_{0.98}$ m^2/L	VOC_{reg} g/L	VOC_{actual} g/L	VOC $H_{0.98}$ g/m^2	liters to hide 32.7 m^2	VOC emitted (g)
11	eggshell	water	34	6.9	8.8	3	0.4	4.77	**14**
12	eggshell	water	33	6.4	8.4	3	0.5	5.14	**15**
13	semigloss	water	33	8	112	41	5.1	4.11	**169**
14	semigloss	water	33	6.9	117	44	6.4	4.77	**210**
15	semigloss	water	33	6.5	68	25	3.8	5.06	**127**
16	semigloss	water	33	6.8	68	25	3.7	4.84	**121**
17	semigloss	water	34	7.3	7.2	2	0.3	4.51	**9**
18	semigloss	water	32	6.2	225	96	15.5	5.31	**509**
19	gloss	water	33	7.2	0	0	0.0	4.57	**0**
20	gloss	water	33	7.2	156	62	8.6	4.57	**283**

VOC Emissions from Coatings

					VOC Measures				
#	type	solvent	%NVV	$H_{0.98}$ m^2/L	VOC_{reg} g/L	VOC_{actual} g/L	VOC $H_{0.98}$ g/m^2	liters to hide 32.7 m^2	VOC emitted (g)
21	flat	solvent	56	5.6	364	364	65.0	5.88	**2139**
22	flat	solvent	55	8.4	370	370	44.0	3.92	**1449**
23	eggshell	solvent	61	6.5	344	344	52.9	5.06	**1741**
24	eggshell	solvent	58	8.6	331	331	38.5	3.83	**1266**
25	eggshell	solvent	70	6.7	247	247	36.9	4.91	**1213**
26	semigloss	solvent	60	7.5	331	331	44.1	4.39	**1452**
27	semigloss	solvent	55	9.1	365	365	40.1	3.62	**1320**
28	semigloss	solvent	77	8.8	200	200	22.7	3.74	**748**
29	gloss	solvent	59	8.9	317	317	35.6	3.70	**1172**
30	gloss	solvent	73	9.1	207	207	22.7	3.62	**748**

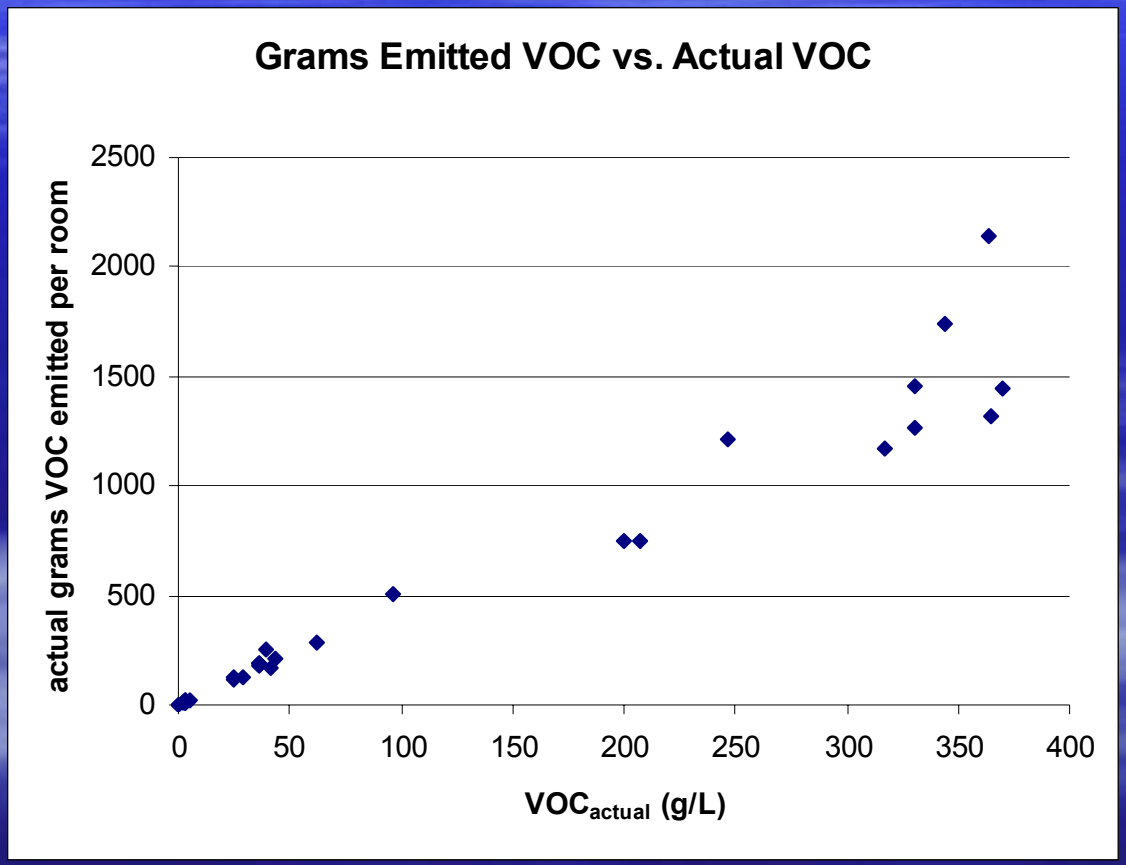
Correlation Between Grams of VOC Emitted and $VOC_{regulatory}$



$VOC_{regulatory}$ is poor predictor of VOC emissions during use

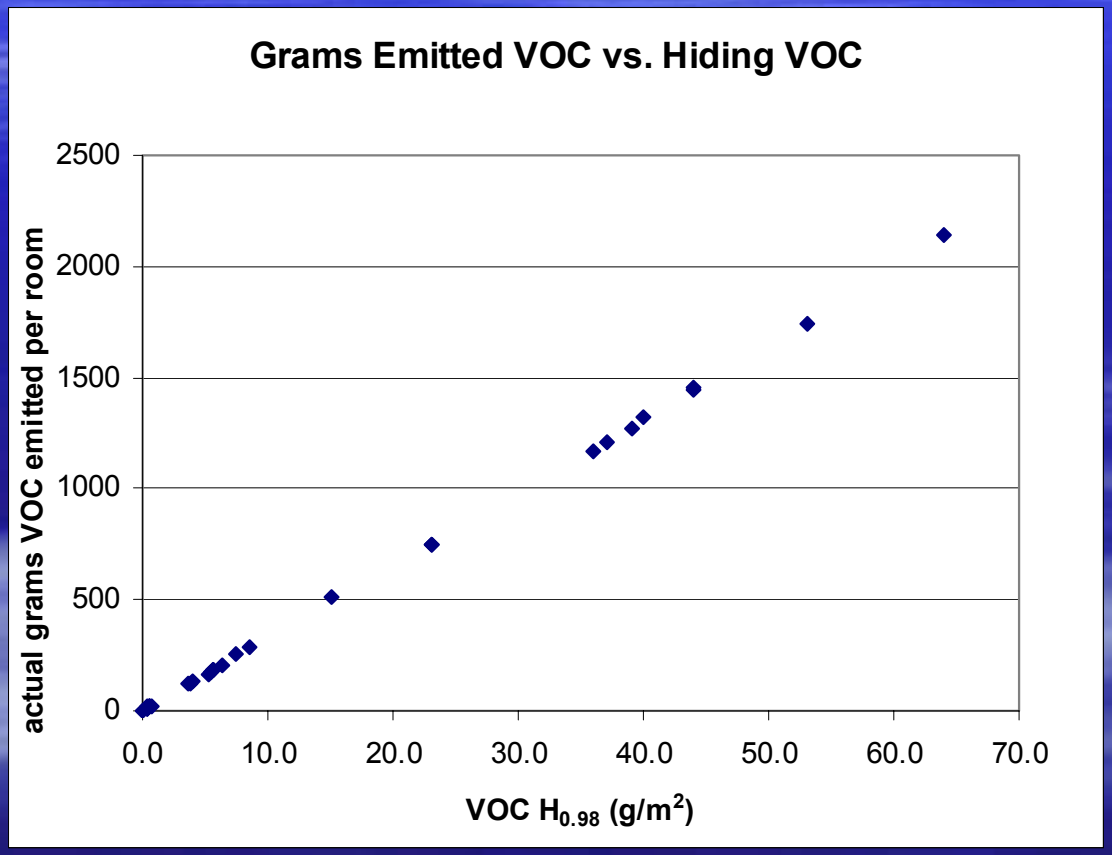
☹

Correlation Between Grams of VOC Emitted and VOC_{actual}



VOC_{actual} is a better, but not perfect predictor of VOC emissions during use

Correlation Between Grams of VOC Emitted and $VOC_{H_{0.98}}$



Hiding VOC is an ideal predictor of VOC emissions during use

☺

Conclusions

- Q. Do solvent-based coatings generally hide better than water-based coatings?
- Answer #1:
  - yes, as formulated
- Answer #2:
  - if “adjusted” to same %NVV, water-based coatings were found to offer better hiding

Conclusions

- Q. Can Kubelka-Munk equations be used to predict hiding for members of a coating family differing in %NVV?
- Answer
  - Yes
  - Comparisons of hiding can be even be made for coatings in different carrier systems (water vs. solvent)

Conclusions

- Q. What factors are important in determining hiding ability of a coating?
- Answer
  - %NVV
  - Nature of solids (pigments, binders, extenders)
  - Carrier appears to play a minor (indirect) role

Conclusions

- Q. How does Hiding VOC relate to other VOC measures for coatings?
- Answer
  - VOC_{actual}
    - describes VOC concentration in liquid coating
    - Is affected by dilution (even with water)
  - $VOC_{regulatory}$
    - For water-based coatings, this measure is often very different from actual VOC content of coating
    - VOC regulatory is not affected by dilution with water
  - Hiding VOC ($VOC_{H0.98}$)
    - A performance-based measure of VOC emissions associated with using a coating
    - Is not affected by dilution

Additional Conclusions

- Higher volume solids does not necessarily produce better hiding
- Not necessarily true that two coats of a 35% NVV WB coating would be needed to hide the same as 1 coat of a 70% NVV SB coating.
- Of coatings tested, SB emissions averaged more than ten times WB emissions, to hide same area
- Suitability of $VOC_{regulatory}$ as a measure called into question, since solids content and hiding were not consistently related

Acknowledgements

- ARB
  - Kevin Cleary
  - Chris Hurley
  - Jim Nyarady
- Cal Poly
  - Dr. Dane Jones
  - Dr. Max Wills
  - Mr. Jon Hurley

CAL POLY