Novel coatings development – the importance of including auxiliary responses

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PPG paints and coatings are used to protect and enhance some of the world's best-known products and brands

World-renowned landmarks

Devices and screens all around you

The planes we fly in – from the windows to the exteriors

Passports and licenses

Cars we drive and the infrastructure to get where we're going

The homes we live in

The offices we work in

The cans we drink from

Agenda

- Industrial Research Methodology
  - What are auxiliary responses?
- Example 1 - New Resin Design for Architectural Coatings
- Example 2 - Protective Coating
- General Observations

DMADV

	Key Questions	Critical for success
Define	What are the goals of the project?	Impactful, clear
Measure	What are the critical to quality characteristics? Are the measurement processes suitable?	Fast, efficient
Analyze	What factors can we change to make improvements?	
Design	What factor combinations lead to optimum performance?	
Verify	Will the product work in the real world?	Cost effective, robust

Filling The Toolbox

- **Critical Thinking**

•SMART Goals
•Thought Map
•Process Map

- **Understanding Variation**

•Control Charts
•Capability & Robust Design
•Special Cause Common Cause
•Components of Variance (COV)
•Measurement System Evaluation (MSE)
•ANOVA (one way; multiple levels)

- **Process Knowledge: Y=f(x)**

DOE Design Tools
- Full & Fractional Factorial
- Mixture / Order of Addition
- Optimal/Custom Design
- Definitive Screening
- Plackett-Burman
- Response Surface

Data Modeling Tools
- Ordinary Least Squares (OLS)
- Normal plots, Pareto & p-values
- Stepwise Regression
- Desirability function (multi-Y)
- Robust Design
- Latent Variable Methods (PCA, PCR, PLS)
- Neural Nets
- Classification & Regression Trees

Simplified Process Map – Automotive Basecoat Development

Make Resin
X – monomer types
X – level of each monomer
X – initiator type
X – feed rates
N – stir speed
y – rheology
y – particle size

Make Basecoat
X – co-resins
X – solvents
X – additives
X – pigments
X – order of addition
N – temperature
y – rheology
y – surface tension

Spray Basecoat
X – air pressure
X – flow rate
X – temperature
X – humidity
X – substrate
N – basecoat age
y – atomization
y – transfer efficiency

Apply Topcoat
X – topcoat type
X – time after basecoat
N – topcoat batch
N – technician
y – wetting
y – penetration

Cure coatings
X – oven temperature
X – time after topcoat
X – orientation
N – airflow
N – oven type
N – contaminates
y – rheology during cure
y – substrate temp. profile

Measure
Y – appearance
Y – colour
Y – humidity resistance
Y – adhesion
y – thermomechanicals
y – microscopy

KEY:
X = Controllable Variable
Y = Main Metric(s)
N = Noise Variable
y = Auxiliary response

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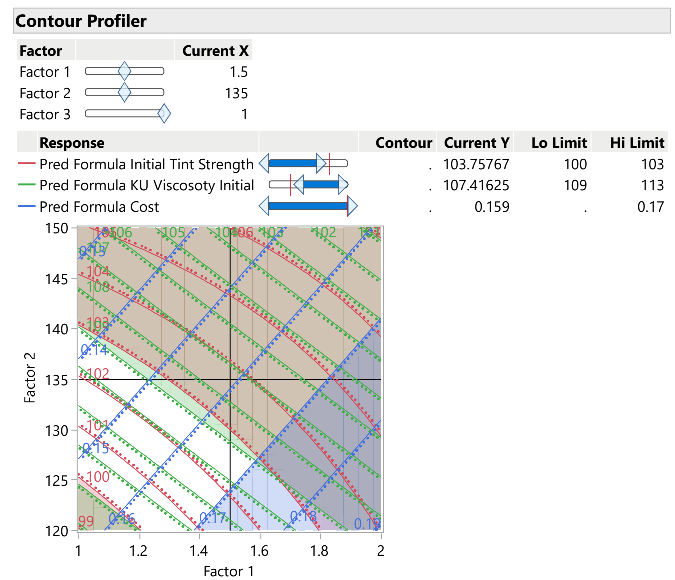
Example 1 – New Resin Design for Architectural Coatings

Goal	New resin for white base paints that meets performance requirements for several global product lines
Initial Status	No single resin meets all requirements. Early Prototypes struggled with low tint strength, poor heat age stability, and poor reproducibility.



Example1 – Resin Location DOE

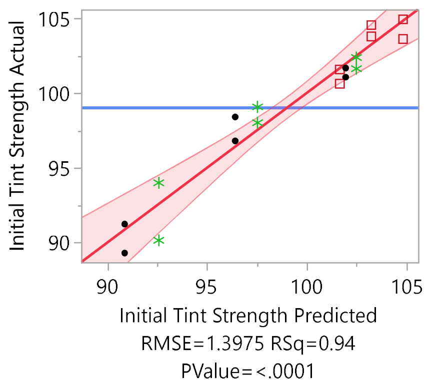
- **Goal**
  - Confirm and quantify previously observed correlation between particle size and tint strength
  - Does co-surfactant addition point affect key properties?
  - Can the resin synthesis be reproduced across three different locations?

	Resin formulation	Target PSz	Co-surfactant addition	reactor location
1	A	150	INITIAL CHARGE	Lab C
2	C	110	INITIAL CHARGE	Lab C
3	D	150	FEED	Lab C
4	B	130	INITIAL CHARGE	Lab C
5	E	130	FEED	Lab C
6	F	110	FEED	Lab C
7	A	150	INITIAL CHARGE	Lab B
8	C	110	INITIAL CHARGE	Lab B
9	D	150	FEED	Lab B
10	B	130	INITIAL CHARGE	Lab B
11	E	130	FEED	Lab B
12	F	110	FEED	Lab B
13	A	150	INITIAL CHARGE	Lab A
14	C	110	INITIAL CHARGE	Lab A
15	D	150	FEED	Lab A
16	B	130	INITIAL CHARGE	Lab A
17	E	130	FEED	Lab A
18	F	110	FEED	Lab A

Example 1

Response Initial Tint Strength

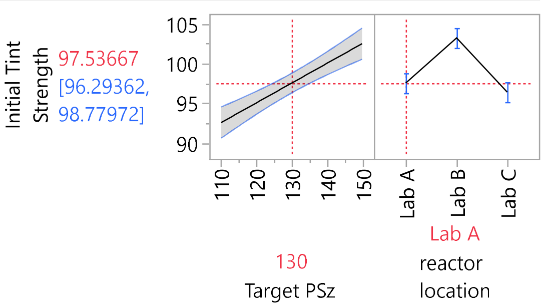
Actual by Predicted Plot

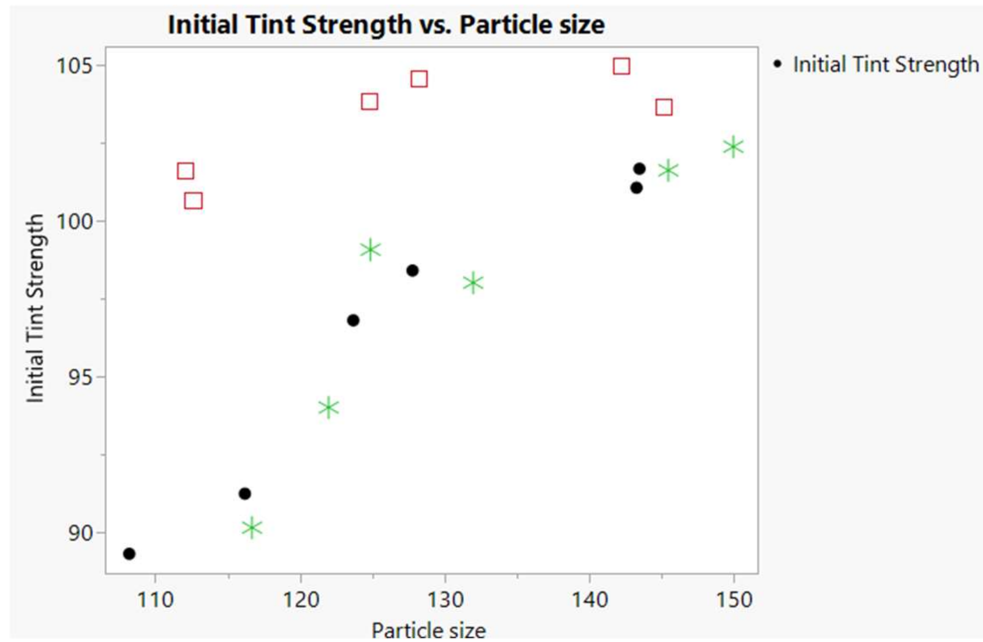


Effect Summary

Source	Logworth	PValue
Target PSz	6.446	0.00000
reactor location	5.361	0.00000
Target PSz*reactor location	2.451	0.00354

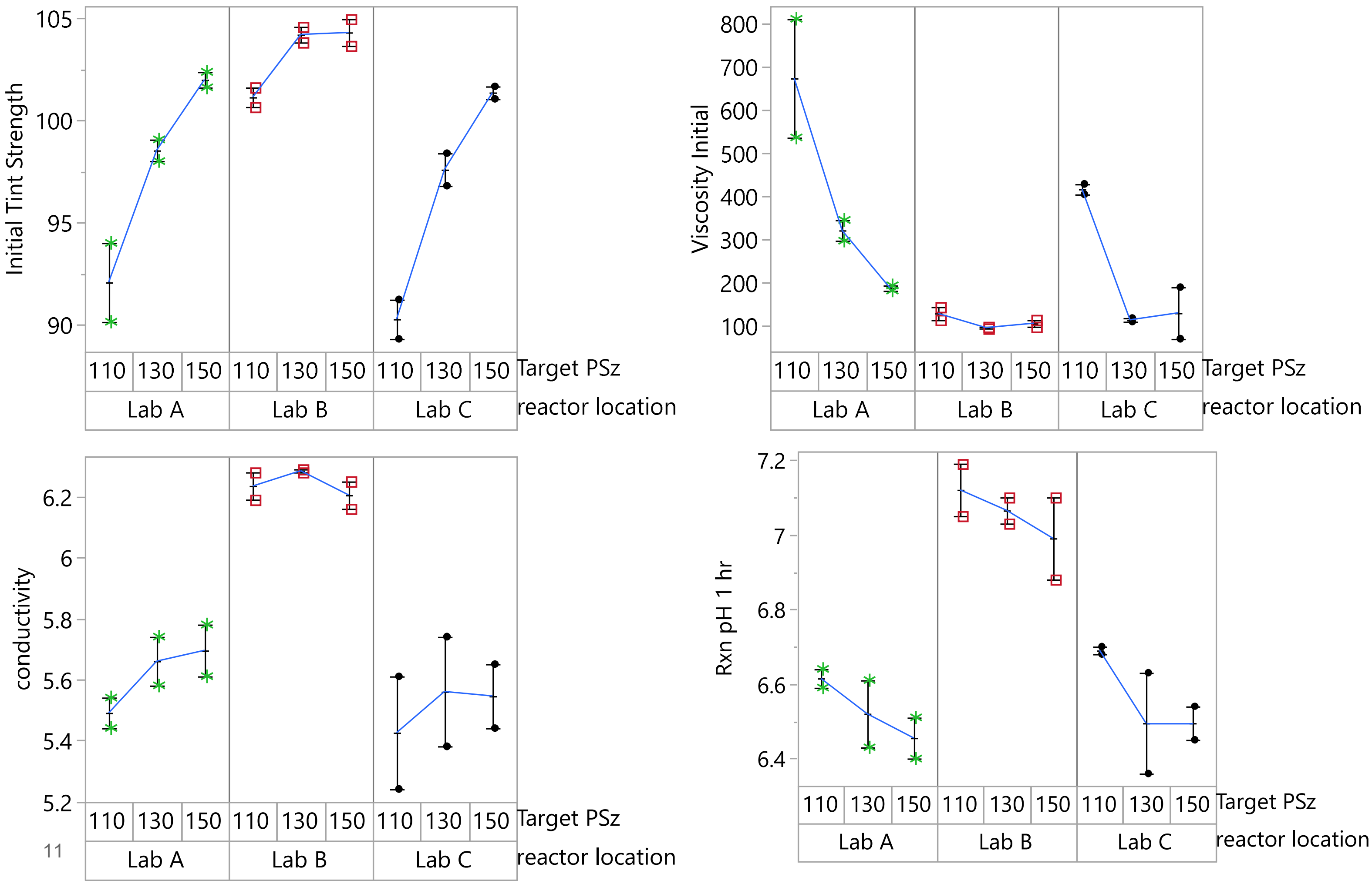
Prediction Profiler





Expected correlation between tint strength and particle size from Labs A and C.
Very different behavior from Lab B.

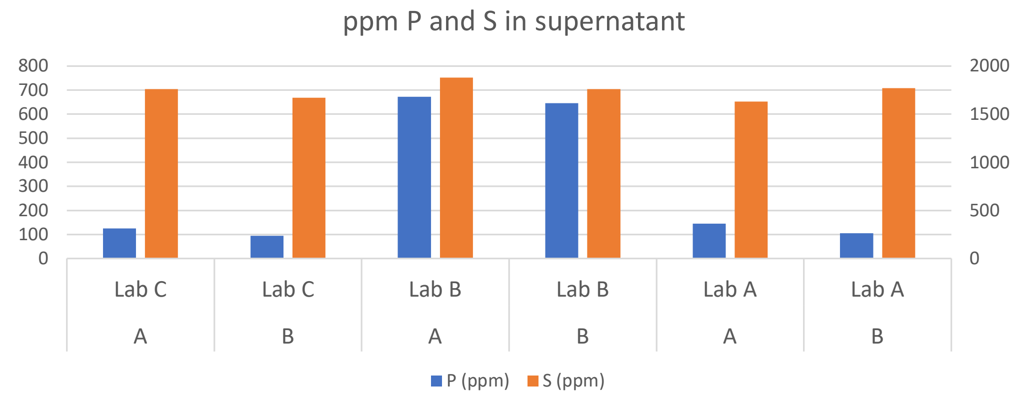
Example 1 – Variability Charts



Resins from Lab B also appear different for other properties.

Example 1 – Resin Location DOE - Conclusions

- What could cause higher conductivity and pH at 1 hr?
  - Analysis of supernatant after precipitation of the polymer

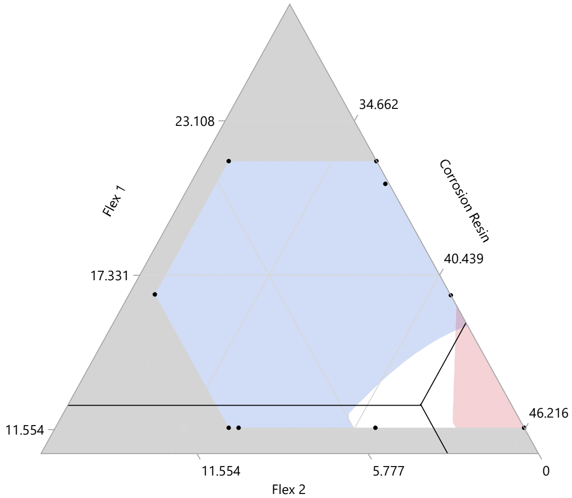


- Resins from Lab B have about 4x the level of P than other labs.
- Only one raw material brings in P
- Further investigation revealed that material supplied to Lab B was too concentrated.

- Auxiliary data from the DOE (little ys) allowed the problem to be identified very quickly.
- Project stayed on track.
- Bonus – a new method of influencing tint strength was identified.

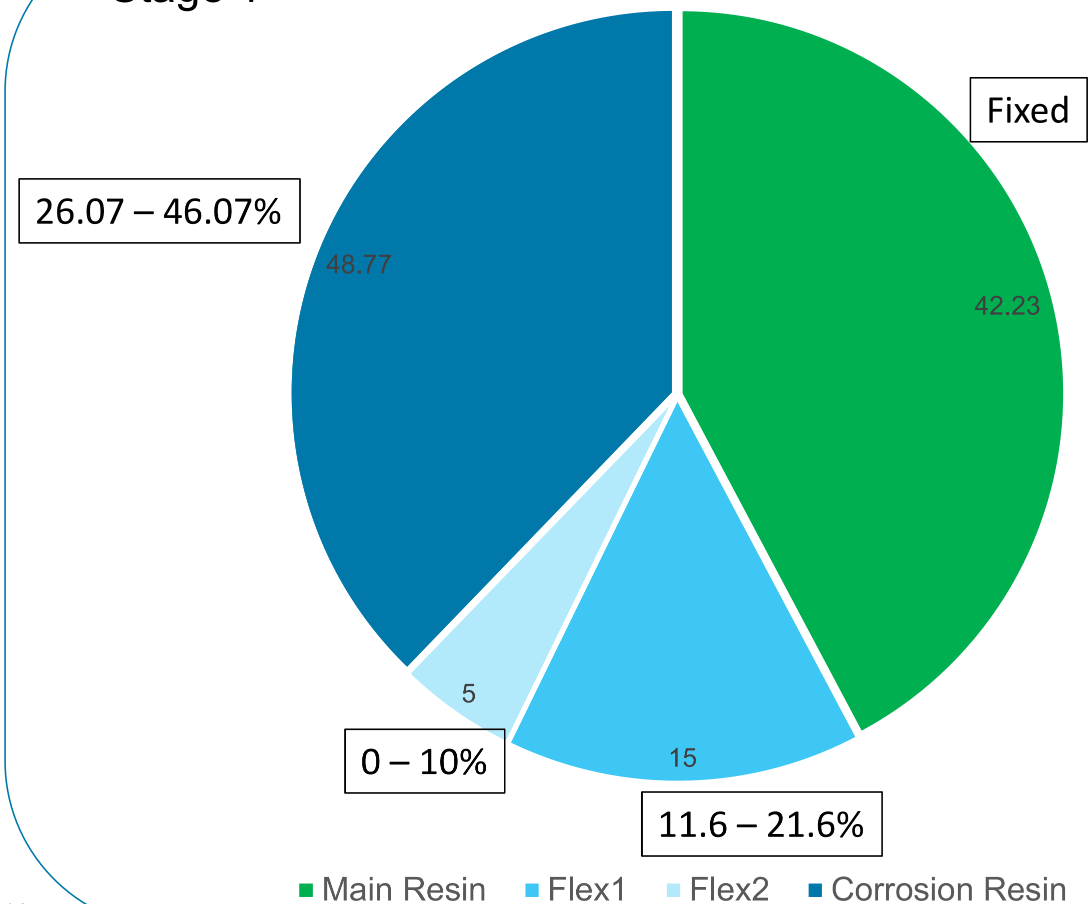
Example 2 – Protective Coating

- Five resin components to be investigated- Corrosion Resin, Flex1, Flex2, Flex3, Flex4
- First three are components incorporated during stage 1 of the coating prep. The other two are added later in a separate step.
- How do the resin components affect corrosion and flexibility?
- What resin levels deliver the best combination of these properties?



Example 2 - Design

Stage 1



Stage 2

+ Flex3

10 – 20%

+ Flex4

0 – 15%

Flex2 + Flex3 >10%

Flex2 + Flex3 <30%

Flex1 + Flex2 + Flex 3 + Flex4 < 41.6%

Flex1 + Flex2 < 26.6%

Building models for mixture + process DOEs

- If interactions between mixture and process variables are unlikely
  - $Y = (a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3) + (b_0 + b_1z_1 + b_2z_2 + b_{12}z_1z_2)$
  - 10 coefficients to determine
- If interactions are possible
  - $Y = (a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3) * (b_0 + b_1z_1 + b_2z_2 + b_{12}z_1z_2)$
  - $Y= b_0 a_1x_1 + b_0 a_2x_2 + b_0 a_3x_3 + b_0 a_{12}x_1x_2 + b_0 a_{13}x_1x_3 + b_0 a_{23}x_2x_3 +$
    $b_1 a_1x_1z_1 + b_1 a_2x_2z_1 + b_1 a_3x_3z_1 + b_1 a_{12}x_1x_2z_1 + b_1 a_{13}x_1x_3z_1 + b_1 a_{23}x_2x_3z_1 +$
    $b_2 a_1x_1z_2 + b_2 a_2x_2z_2 + b_2 a_3x_3z_2 + b_2 a_{12}x_1x_2z_2 + b_2 a_{13}x_1x_3z_2 + b_2 a_{23}x_2x_3z_2 +$
    $b_{12} a_1x_1z_1z_2 + b_{12} a_2x_2z_1z_2 + b_{12} a_3x_3z_1z_2 + b_{12} a_{12}x_1x_2z_1z_2 + b_{12} a_{13}x_1x_3z_1z_2 + b_{12} a_{23}x_2x_3z_1z_2$
  - 24 coefficients to determine for the full model

Example 2 - DOE

Factors

Add N Factors 1

Name	Role	Changes	Values
Corrosion Resin	Mixture	Easy	26.07 46.07
Flex1	Mixture	Easy	11.6 21.6
Flex2	Mixture	Easy	0 10
Flex3	Continuous	Easy	10 20
Flex4	Continuous	Easy	0 15

Covariate/Candidate Runs

Load a set of candidate runs for covariates from the current data table.

Define Factor Constraints

- ○ None
- ◉ Specify Linear Constraints
- ○ Use Disallowed Combinations Filter
- ○ Use Disallowed Combinations Script

Linear Constraints

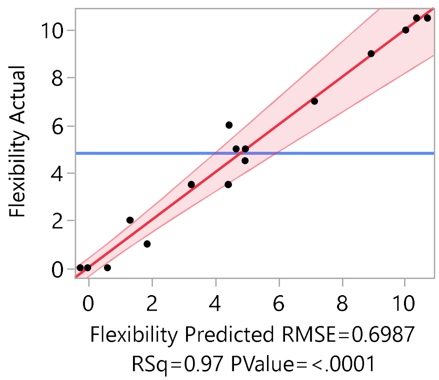
0 Corrosion Resin +	0 Flex1 +	0 Flex2 +	1 Flex3 +	1 Flex4	≥	10
0 Corrosion Resin +	0 Flex1 +	0 Flex2 +	1 Flex3 +	1 Flex4	≤	30
0 Corrosion Resin +	1 Flex1 +	1 Flex2 +	1 Flex3 +	1 Flex4	≤	41.5
0 Corrosion Resin +	1 Flex1 +	1 Flex2 +	0 Flex3 +	0 Flex4	≤	26.6

	Flex 1	Flex 2	Corrosion Resin	Flex 3	Flex 4
	21.6	10	46.2	20	15
	11.6	0	31.2	10	0
1	11.6	0	46.17	10	10
2	11.6	0	46.17	10	15
3	11.6	0	46.17	15	5
4	11.6	0	46.17	20	0
5	11.6	0	46.17	20	10
6	11.6	5.04	41.13	18.48	6.48
7	11.6	9.67	36.5	20	0.32
8	11.6	10	36.17	10	10
9	16.57	0	41.2	10	15
10	16.6	10	31.17	10	5
11	16.6	10	31.17	15	0
12	20.74	0.13	36.9	10	10.73
13	21.6	0	36.17	10	0
14	21.6	0	36.17	10	10
15	21.6	0	36.17	20	0
16	21.6	5	31.17	12.11	2.62

Example 2 - Models

Response Flexibility

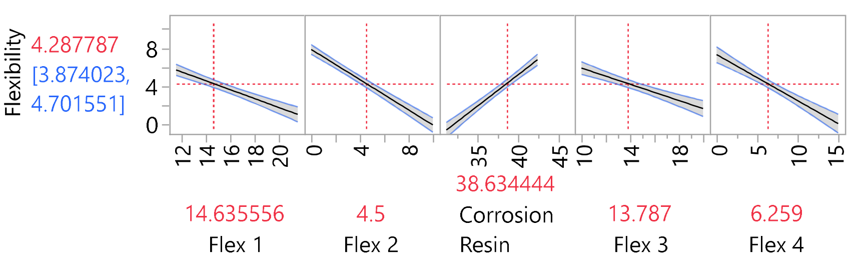
Actual by Predicted Plot



Summary of Fit

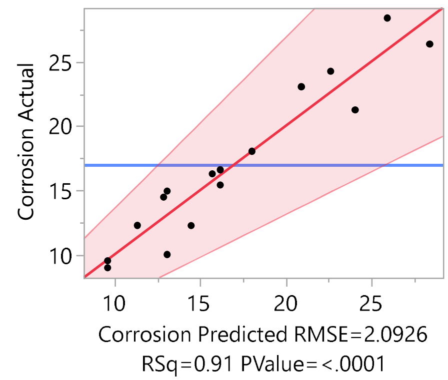
RSquare	0.97453
RSquare Adj	0.965268
Root Mean Square Error	0.698741
Mean of Response	4.84375
Observations (or Sum Wgts)	16

Prediction Profiler



Response Corrosion

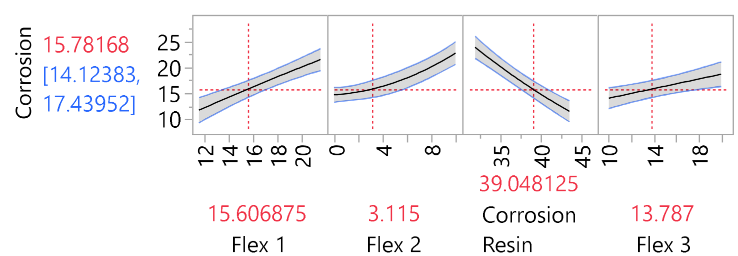
Actual by Predicted Plot



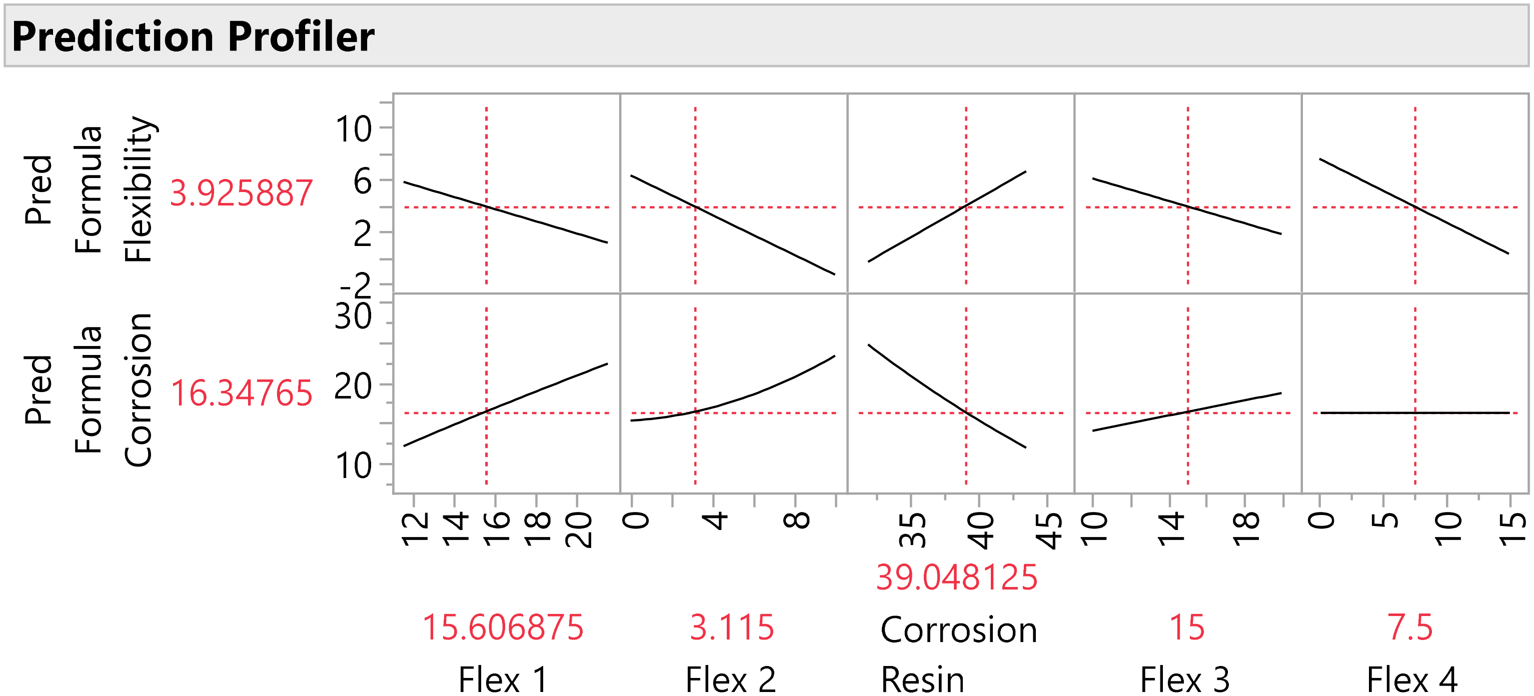
Summary of Fit

RSquare	0.913359
RSquare Adj	0.881853
Root Mean Square Error	2.092603
Mean of Response	16.99125
Observations (or Sum Wgts)	16

Prediction Profiler



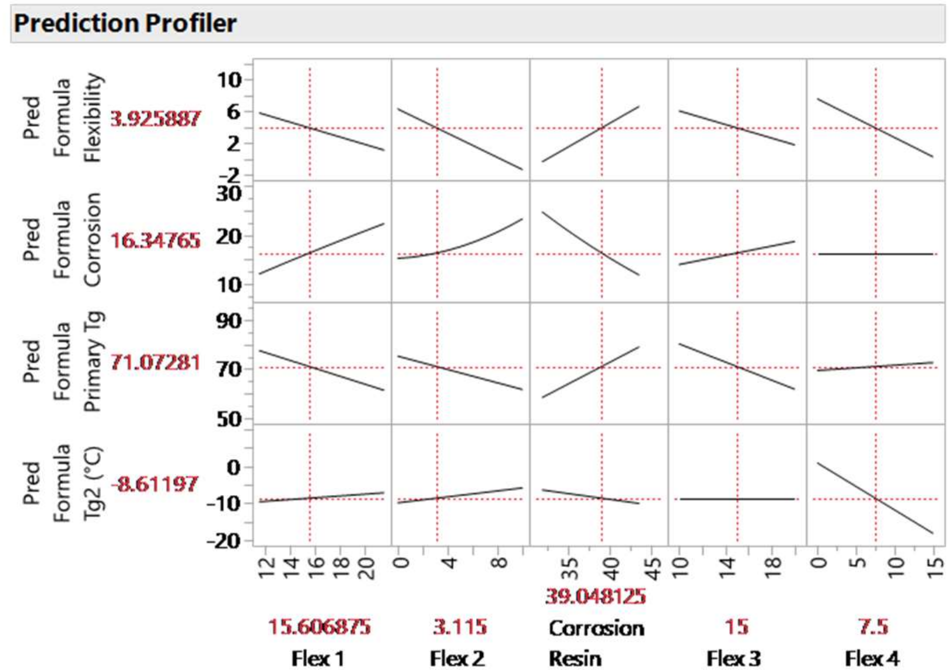
Example 2 – Balancing corrosion and flexibility



- As expected, corrosion and flexibility are inversely correlated
- .
- Flex 4 shows unusual behavior
- Higher levels improve flexibility but do not hurt corrosion
- Why?

Pairwise Correlations

Variable	by Variable	Correlation
Tg2 (°C)	Flex 4	-0.9238
Corrosion	Corrosion Resin	-0.8667
Stress at Max Load	Tg2 (°C)	0.8653
Primary Tg	Corrosion	-0.8577
Flexibility	Flex 2	-0.8052
Tg2 (°C)	Primary Tg	-0.8011
Stress at Max Load	Primary Tg	-0.7929
Youngs Modulus	Tg2 (°C)	0.7918
T cure	Corrosion Resin	0.7757
Corrosion	Flexibility	-0.7667

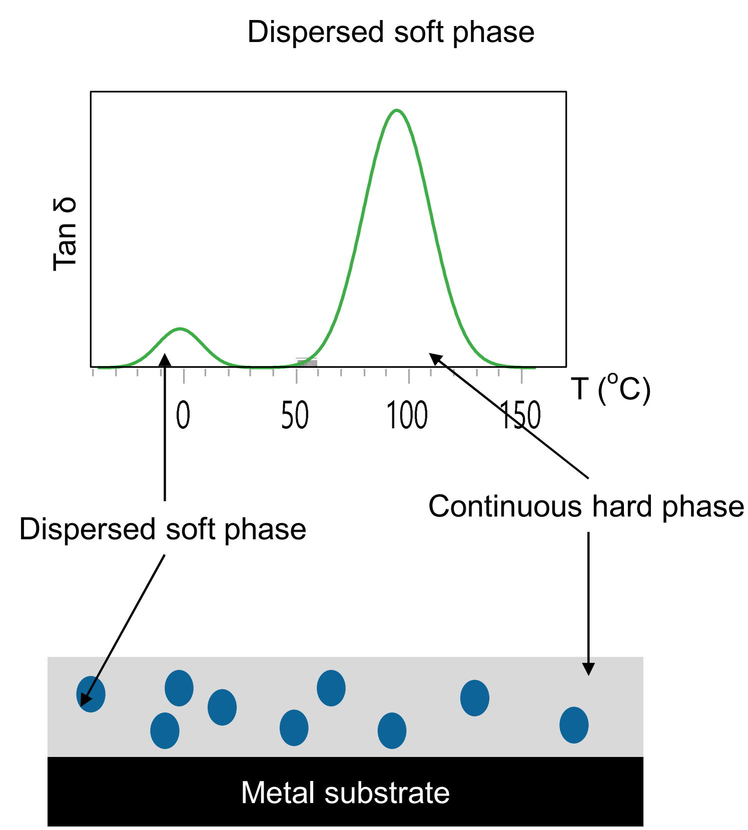


- Flex 4 level shows strong correlation with Tg2

- Need to increase primary Tg to improve corrosion
- Need to decrease primary Tg to improve flexibility
  - Except for Flex 4 – allows flexibility to be improved without decreasing Primary Tg
- Flex 4 provides a way out of the flexibility/corrosion compromise

Example 2 - Learnings

- Multiple Tgs are usually a sign of a multi-phase material
  - Confirmed by microscopy
- High Tg of the continuous phase provides good corrosion resistance
- Soft dispersed phase contributes to flexibility



Conclusions

- It is possible to carry out successful DOEs where only the critical responses are measured (Ys), but…

- Including carefully selected auxiliary responses (ys) can often be very valuable.
  - Bring clarity to unexpected results
  - Build scientific knowledge
  - Simpler or better test methods

- JMP provides many tools to help with this

- We thank the many associates at PPG's Coatings Innovation Centre who contributed to this work.