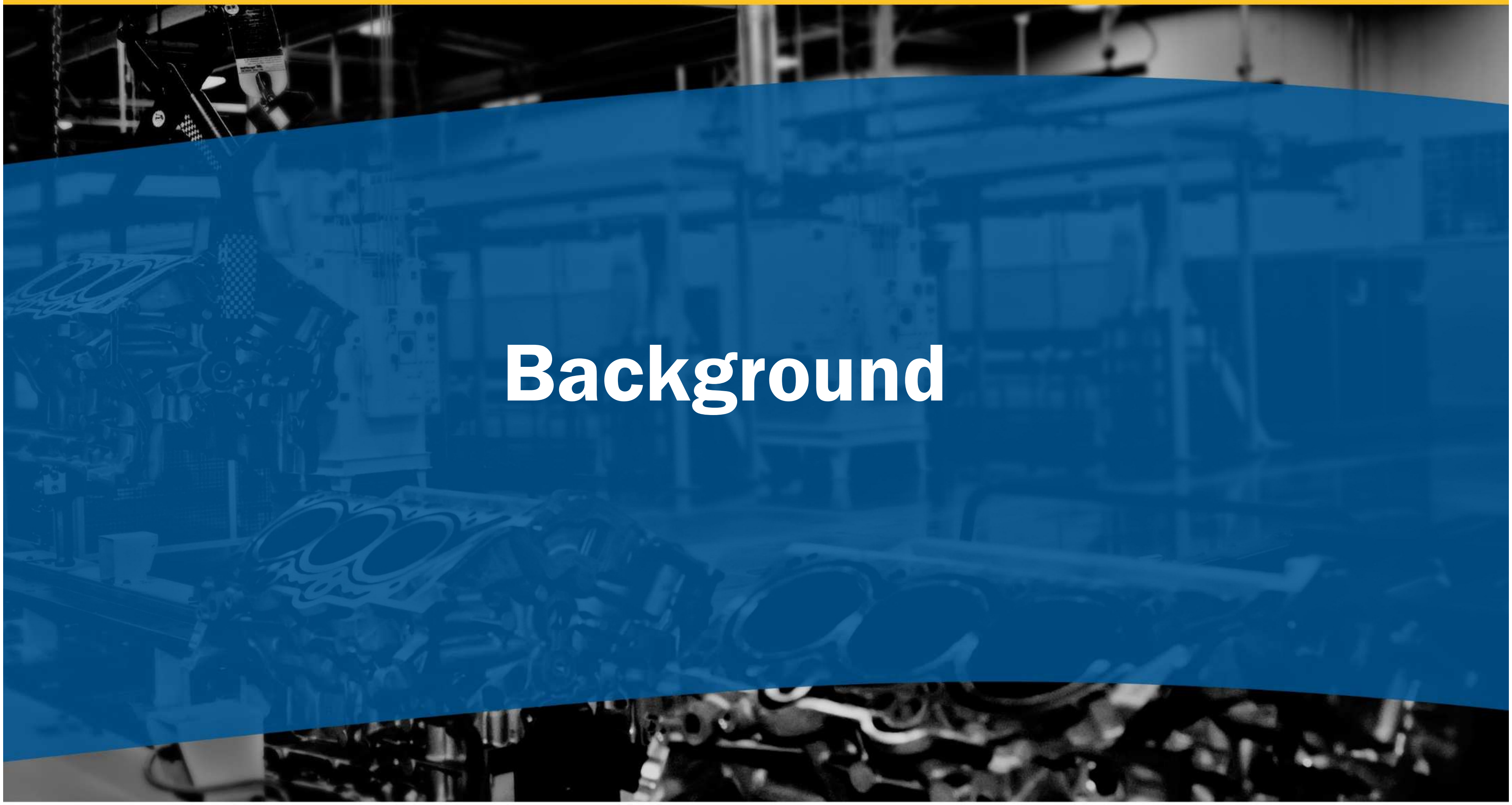
It's what's inside that counts.

Using Experimental Design and Statistical Software to Investigate the Impact of Amines on Metalworking Fluid Lubricity

Jason Pandolfo
19JUN2019

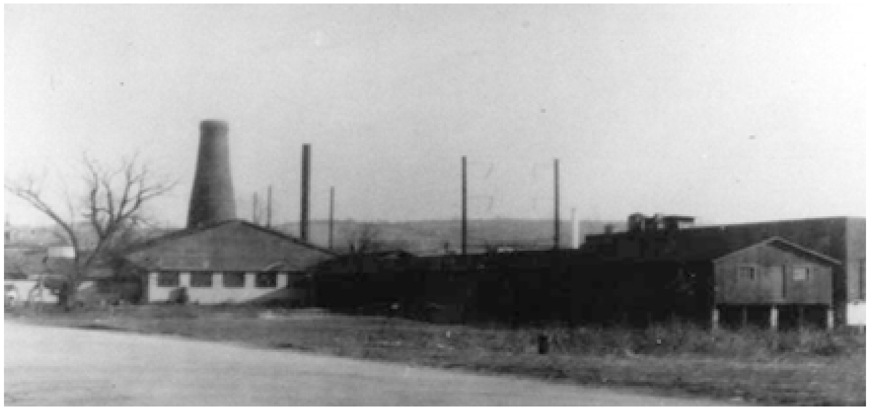
Background



About Quaker Chemical Corp.

Quaker
It's what's inside that counts.™

- Global Headquarters: Conshohocken, PA
- Supplier of industrial process fluids since 1918
- 2,160 associates worldwide
- 26 locations in 21 countries
- 2018 sales: $867.5m
- 2018 R&D expenditures: $24.5m



Metalworking Fluids

- Oil emulsified in water
- Cools and lubricates tool and part
- Extends tool life
- Removes chips and debris
- Prevents rust and corrosion

http://www.fabricatingandmetalworking.com/2015/06/a-new-wave-of-metalworking-fluids/

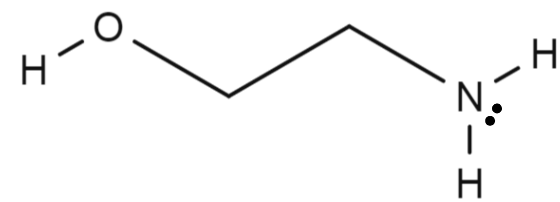
Metalworking Fluids

MWF Composition

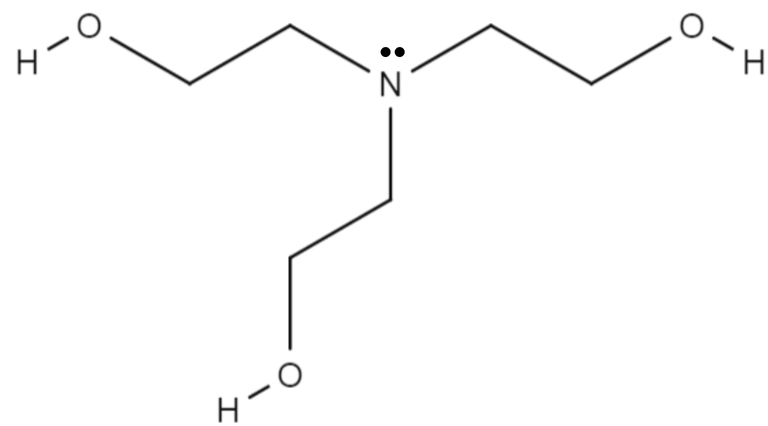
- Carrier oil: 20-50%
- Lubricity additives: 5-15%
- Surfactants:
  - Fatty acids: 5-15%
  - Emulsifiers: 5-15%
- Amines: 5-15%
- Corrosion inhibitors: 1-5%
- Biocides: 0.5-5%

Amines

- Weak bases
- React with fatty acids and other acid species
- Maintain pH at ~9.2—9.5
- Help to prevent biological growth in emulsions
- Aid in corrosion resistance
- ***Provide lubricity***



Mono-ethanolamine (MEA)



Tri-ethanolamine (TEA)

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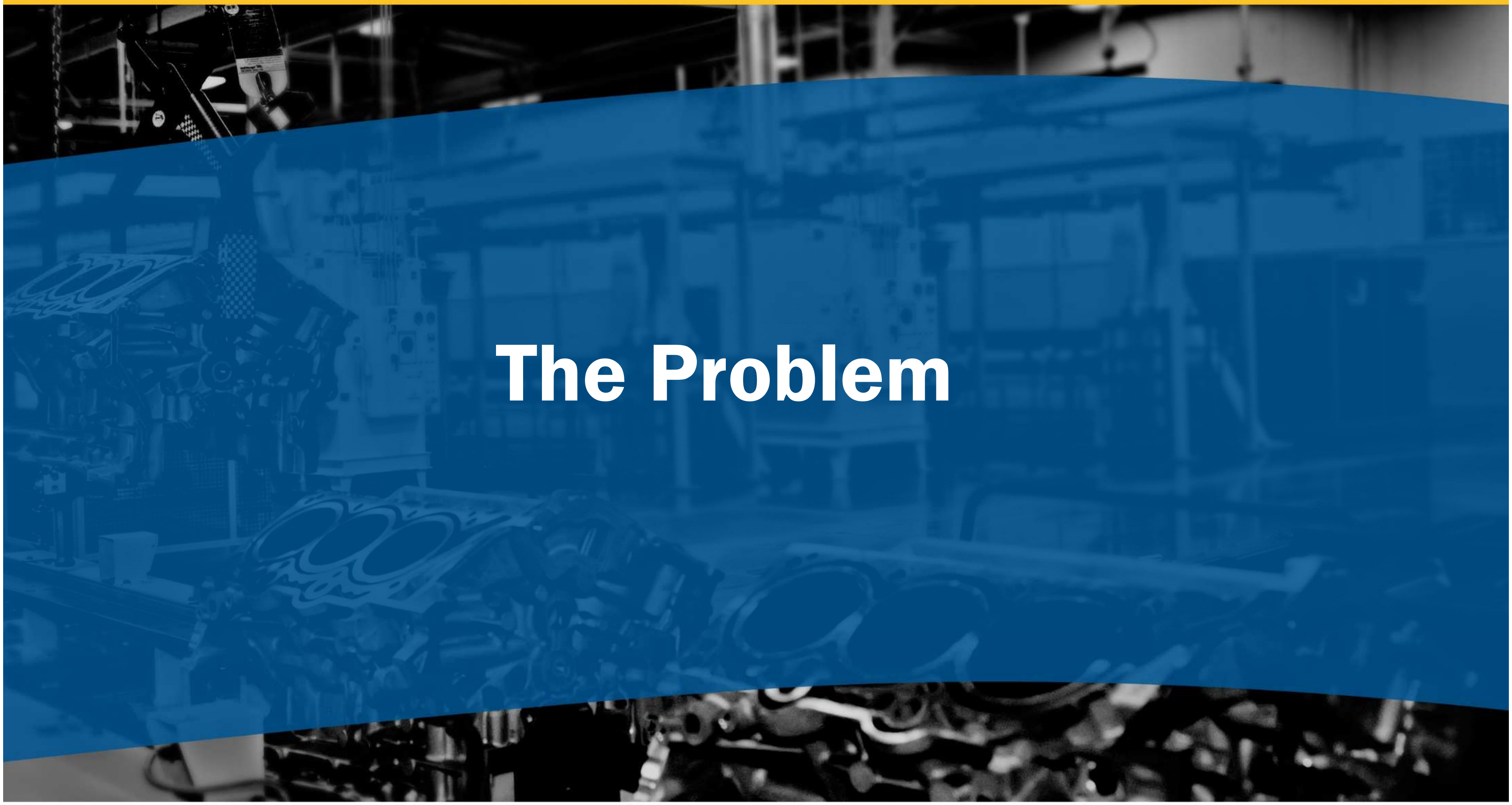

The Problem

Modifying an Existing Product

- "Product A" needed to be modified:
  - Improve pH buffering
  - Reduce raw material cost
  - Maintain overall performance
- Formulated "Product B"
  - Like-for-like swaps, cost rebalancing
  - Changed the amine package
- Product B was not the same as Product A:
  - Lubricity was noticeably worse
  - Product A tapping torque: ~160 N-cm
  - Product B tapping torque: ~185 N-cm

Comparing the Products

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Both products were similar:

Raw Material	Product A	Product B
Carrier Oil	Moderately Expensive	Similar, less expensive
Lubricity Additives	No changes	
Fatty Acids	No changes	
Emulsifiers	6.5% fatty alcohol	4.0% fatty alcohol
	Expensive ethoxylated emulsifier	Less expensive ethoxylated emulsifier
	—	Additional emulsifier (1.0%)
Amine Package	Needed Improvement	More amine, better performance

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Total Amine Milli-equivalents	108.8	135.9

What is Degrading Lubricity?

- An initial investigation was conducted
- Turned to OFAT experimentation first:
  - Looking for a quick-fix
  - Same amount of fatty alcohol : **Product B still worse**
- Used DOE to investigate:
  - Rebalancing the emulsifier package : **no effect**
  - Rebalancing the fatty acid & emulsifiers : **no effect**
- ***We needed to take a different approach!***

The Investigation

Re-Examine the Differences

- Four things to investigate:
  - Difference between carrier oils
  - The amine packages
  - Difference between ethoxylated emulsifiers
  - The additional emulsifier in Product B
- We set up a factorial experiment to examine the drivers

Factor	Low (Product A)	High (Product B)
Carrier Oil	Expensive	Cheap
Amine Package	Product A	Product B
Ethoxylated Emulsifier	Expensive	Cheap
Additional Emulsifier	0	1.0%

- 16 samples, no replicates, no center points

The MicroTap LabTap II G8:

Instrument Highlights:

- Torque range: 50-700 N-cm
- Spindle speed: 300-3000 RPM
- Max thread depth: 45 mm
- Variety of aluminum/steel alloys
- Range of spindles: M2.5-M10
- Cutting and forming operation
- Operational and statistical software

- ***Quantitative response (N-cm)***
- ***High-precision***

Factorial Results

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Model with ABCD Term Removed:

Response 1: Tapping Torque

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	416.22	14	29.73	2.68	0.4492	not significant
A-Carrier Oil	6.25	1	6.25	0.5625	0.5903	
B-Amine Pkg.	330.03	1	330.03	29.70	0.1155	
C-Ethoxylated Surf.	0.4444	1	0.4444	0.0400	0.8743	
D-Add'l Eth. Surf	16.00	1	16.00	1.44	0.4423	
AB	5.44	1	5.44	0.4900	0.6112	
AC	20.25	1	20.25	1.82	0.4059	
AD	4.69	1	4.69	0.4225	0.6331	
BC	0.0278	1	0.0278	0.0025	0.9682	
BD	0.2500	1	0.2500	0.0225	0.9052	
CD	9.00	1	9.00	0.8100	0.5335	
ABC	0.1111	1	0.1111	0.0100	0.9365	
ABD	1.00	1	1.00	0.0900	0.8145	
ACD	14.69	1	14.69	1.32	0.4557	
BCD	8.03	1	8.03	0.7225	0.5515	
Residual	11.11	1	11.11			
Cor Total	427.33	15				

Factorial Results

Model with Main & 2-Factor Interactions:

Response 1: Tapping Torque

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	392.39	10	39.24	5.61	0.0353	significant
A-Carrier Oil	6.25	1	6.25	0.8943	0.3877	
B-Amine Pkg.	330.03	1	330.03	47.22	0.0010	
C-Ethoxylated Surf.	0.4444	1	0.4444	0.0636	0.8109	
D-Add'l Eth. Surf	16.00	1	16.00	2.29	0.1907	
AB	5.44	1	5.44	0.7790	0.4179	
AC	20.25	1	20.25	2.90	0.1495	
AD	4.69	1	4.69	0.6717	0.4497	
BC	0.0278	1	0.0278	0.0040	0.9522	
BD	0.2500	1	0.2500	0.0358	0.8574	
CD	9.00	1	9.00	1.29	0.3079	
Residual	34.94	5	6.99			
Cor Total	427.33	15				

Barely significant

Factorial Results

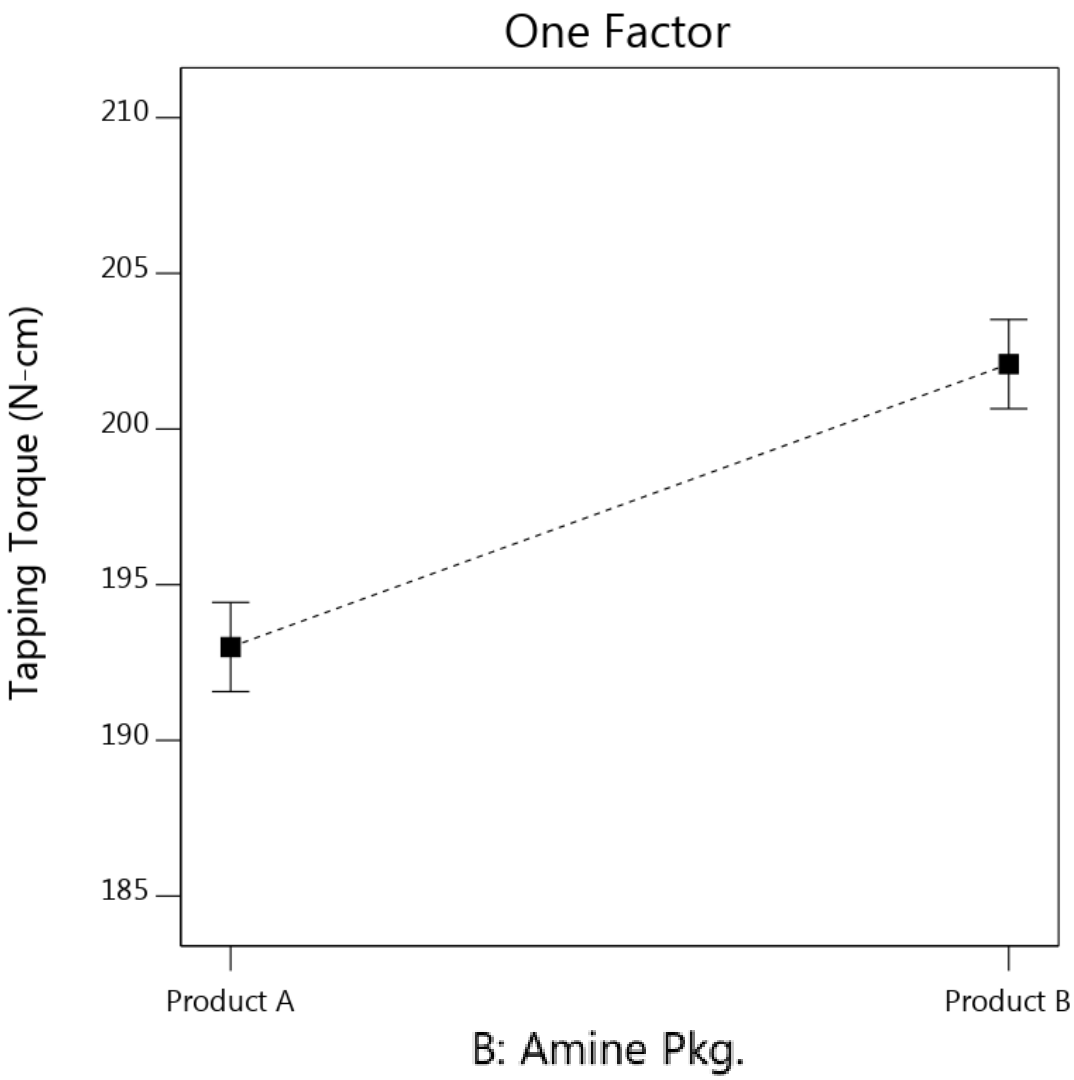
Main Effects Model:

Response 1: Tapping Torque

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	352.72	4	88.18	13.00	0.0004	significant
A-Carrier Oil	6.25	1	6.25	0.9214	0.3577	
B-Amine Pkg.	330.03	1	330.03	48.66	< 0.0001	
C-Ethoxylated Surf.	0.4444	1	0.4444	0.0655	0.8027	
D-Add'l Eth. Surf	16.00	1	16.00	2.36	0.1528	
Residual	74.61	11	6.78			
Cor Total	427.33	15				

Std. Dev.	2.60		**R^2**	0.8254
Mean	199.33		**Adjusted R^2**	0.7619
C.V. %	1.31		**Predicted R^2**	0.6306
			Adeq Precision	8.7003

Factorial Results



Further Exploration

The Starting Point

- Amines are affecting machining performance
- Questions that arose:
  - Which amines are having the strongest effect?
  - Does total amine make a difference?
  - Can we tailor amine packages to desired performance?
- The best way to answer these questions was with a mixture design

The Design

- ***Investigating 6 amines:***
  - 3 are in Product B
  - 3 are new amines
  - *Not investigating the amine package of Product A*
- Formulating to a total of 135.9 amine milli-equivalents
- Assessing each amine over a different range:
  - Based on usage guidelines
- Experimental logistics:
  - Optimal design setup with Design-Expert® software
  - Augmented simplex lattice
  - Additional lack of fit points for better coverage
  - 2 blocks of 22 samples each
  - *Adequate fraction of design space (FDS)*

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  ➢ *Not investigating the amine package of Product A*

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  - ***Adequate fraction of design space (FDS)***

The "Dummy Factor"

- A mixture-amount technique
- Allows us to vary the total amount of material
- Adds one extra component to the experiment
- Does not contribute active material
  - Adds inert material
  - Reduces the total active material

Dummy %	Active %	Perceived Total %
0	100	100
5	95	100
10	90	100
⋮	⋮	⋮

Experimental Setup

Component	Low	High
Amine A	0	82.0
Amine B	0	42.7
Amine C	0	27.6
Amine D	15.2	30.5
Amine E	0	22.5
Amine F	0	39.7
Dummy	0	67.95
Total	*135.9 milli-equivalents*	

Experimental Results

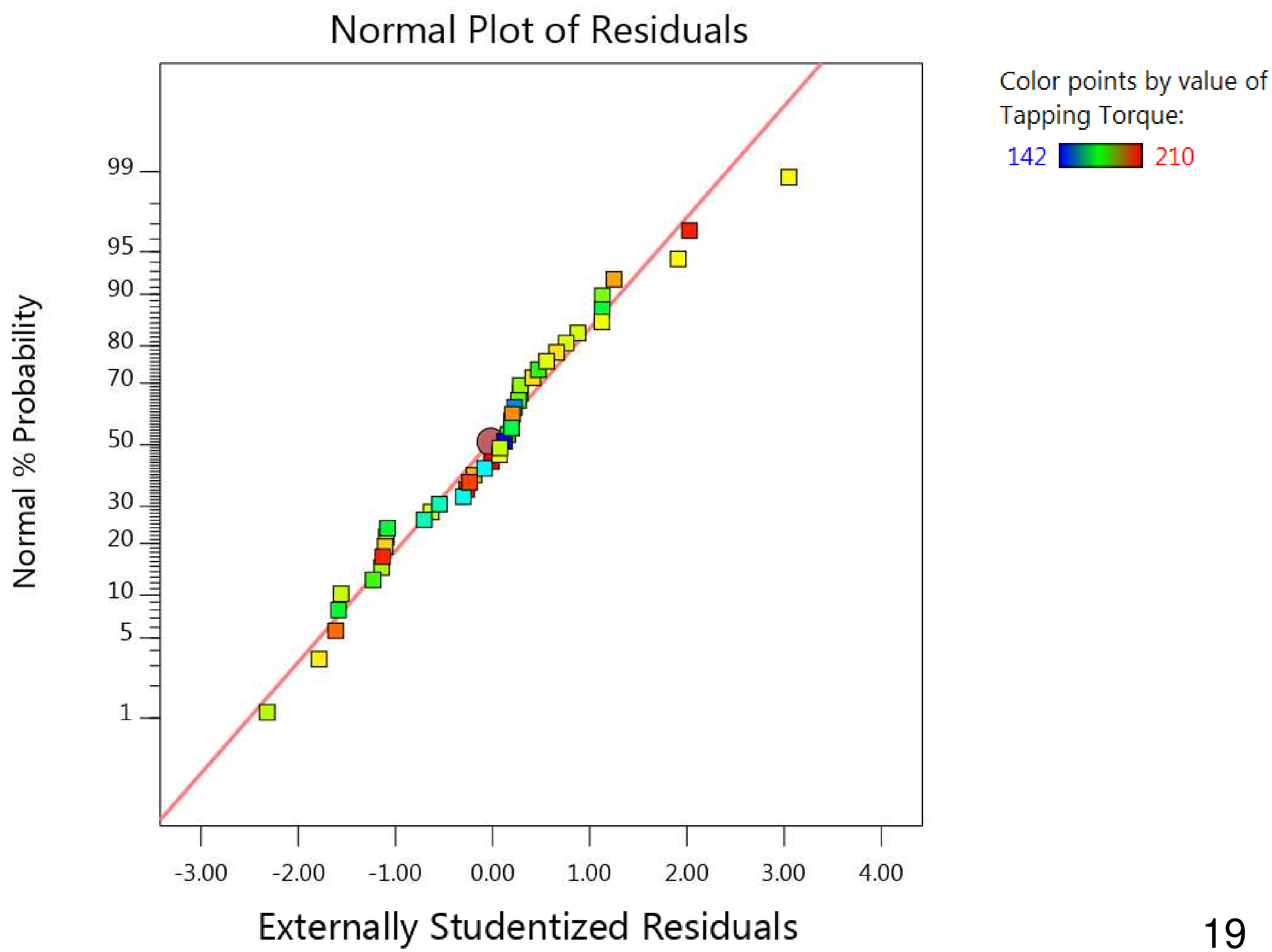
Reduced Special Cubic Model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Block	37.59	1	37.59			
Model	10795.21	23	469.36	115.90	< 0.0001	significant
[1]Linear Mixture	8825.42	6	1470.90	363.20	< 0.0001	
AB	0.2477	1	0.2477	0.0612	0.8073	
AC	192.90	1	192.90	47.63	< 0.0001	
AD	180.12	1	180.12	44.48	< 0.0001	
AE	4.63	1	4.63	1.14	0.2984	
AF	149.20	1	149.20	36.84	< 0.0001	
AG	121.53	1	121.53	30.01	< 0.0001	
BC	214.16	1	214.16	52.88	< 0.0001	
BD	85.22	1	85.22	21.04	0.0002	
BE	4.16	1	4.16	1.03	0.3234	
BG	85.20	1	85.20	21.04	0.0002	
CD	339.67	1	339.67	83.87	< 0.0001	
CE	35.54	1	35.54	8.78	0.0080	
CF	13.64	1	13.64	3.37	0.0822	
CG	47.29	1	47.29	11.68	0.0029	
DF	18.29	1	18.29	4.52	0.0469	
ABD	125.85	1	125.85	31.08	< 0.0001	
ABE	44.10	1	44.10	10.89	0.0038	
Residual	76.95	19	4.05			
Lack of Fit	57.56	15	3.84	0.7916	0.6725	not significant
Pure Error	19.39	4	4.85			
Cor Total	10909.74	43				

Std. Dev.	2.01	**R^2**	0.9929
Mean	186.64	**Adjusted R^2**	0.9844
C.V. %	1.08	**Predicted R^2**	0.9537
		Adeq Precision	44.9299

Response 1: Tapping Torque

Experiment Diagnostics



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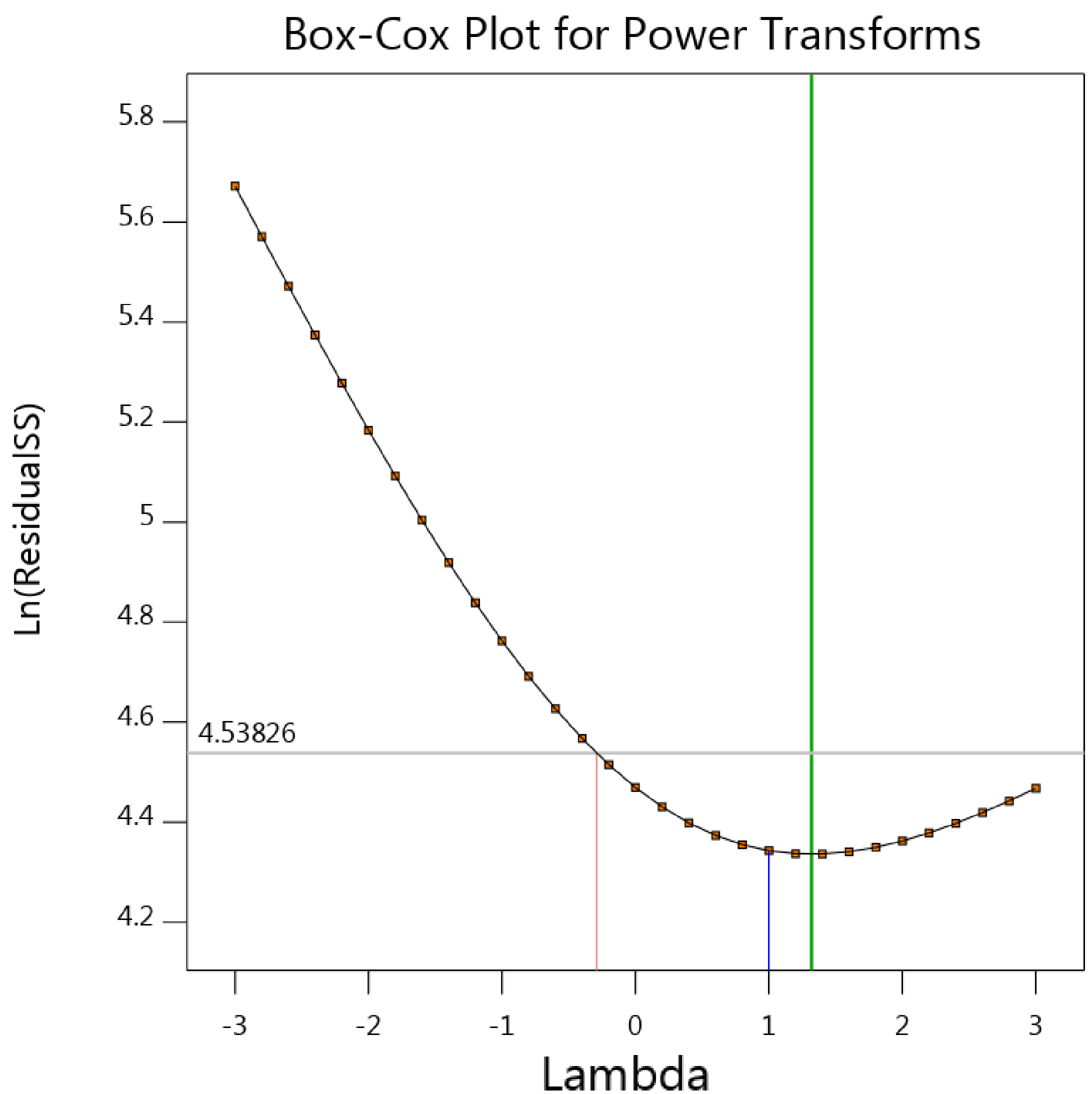
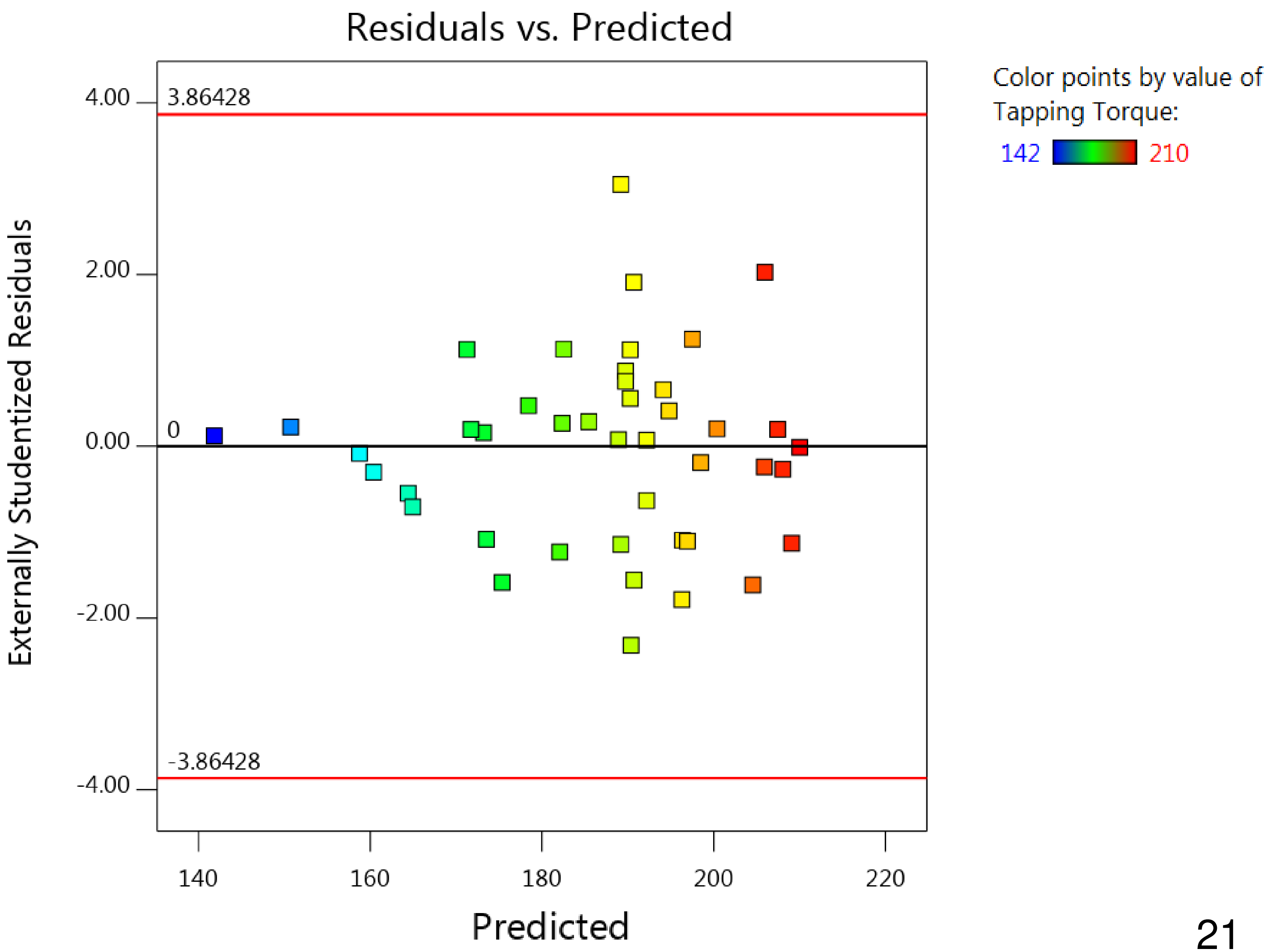


Current Lambda = 1
Best Lambda = 1.32
CI for Lambda: (-0.29, 3.5)

Recommended transform:
None
(Lambda = 1)

Experiment Diagnostics



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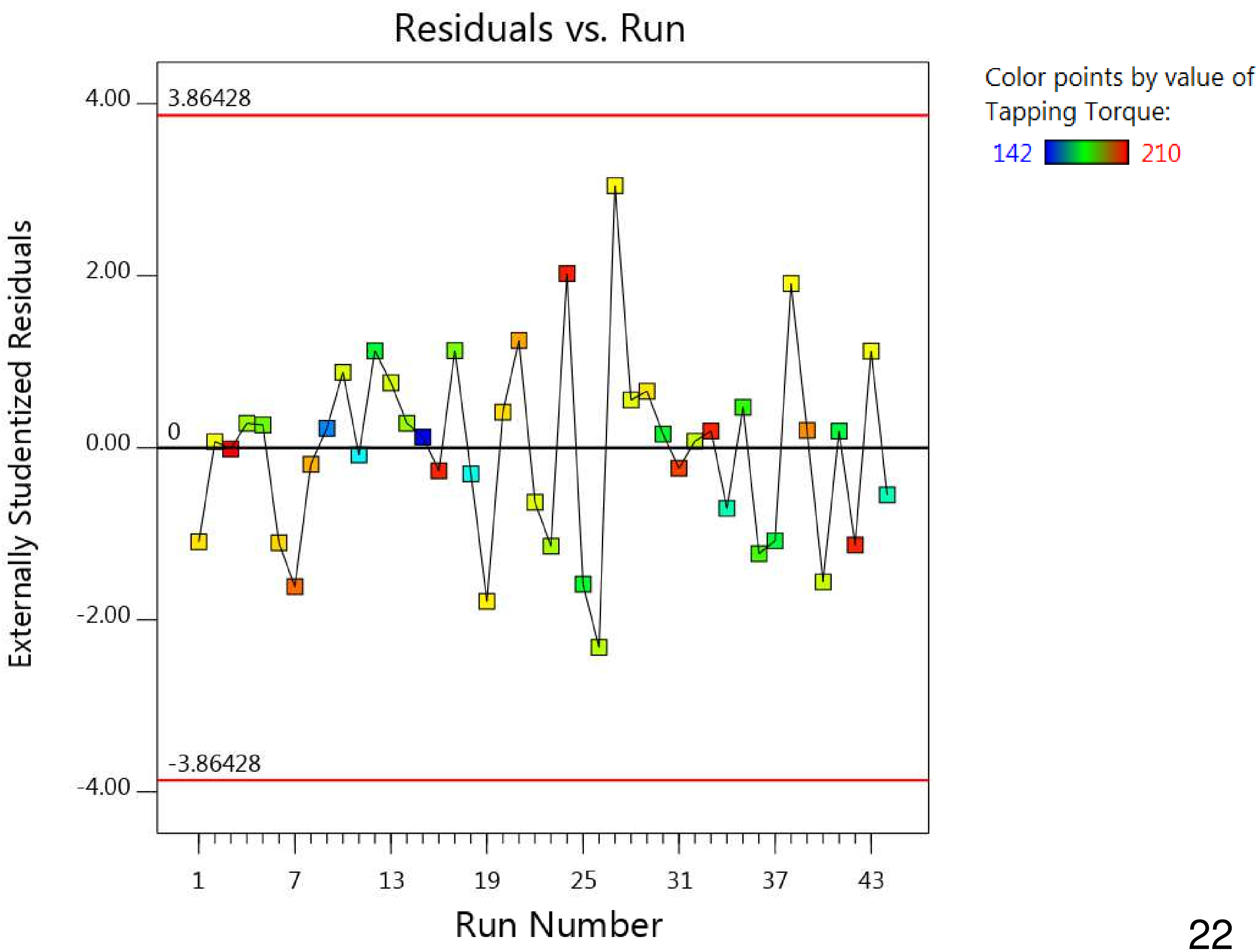

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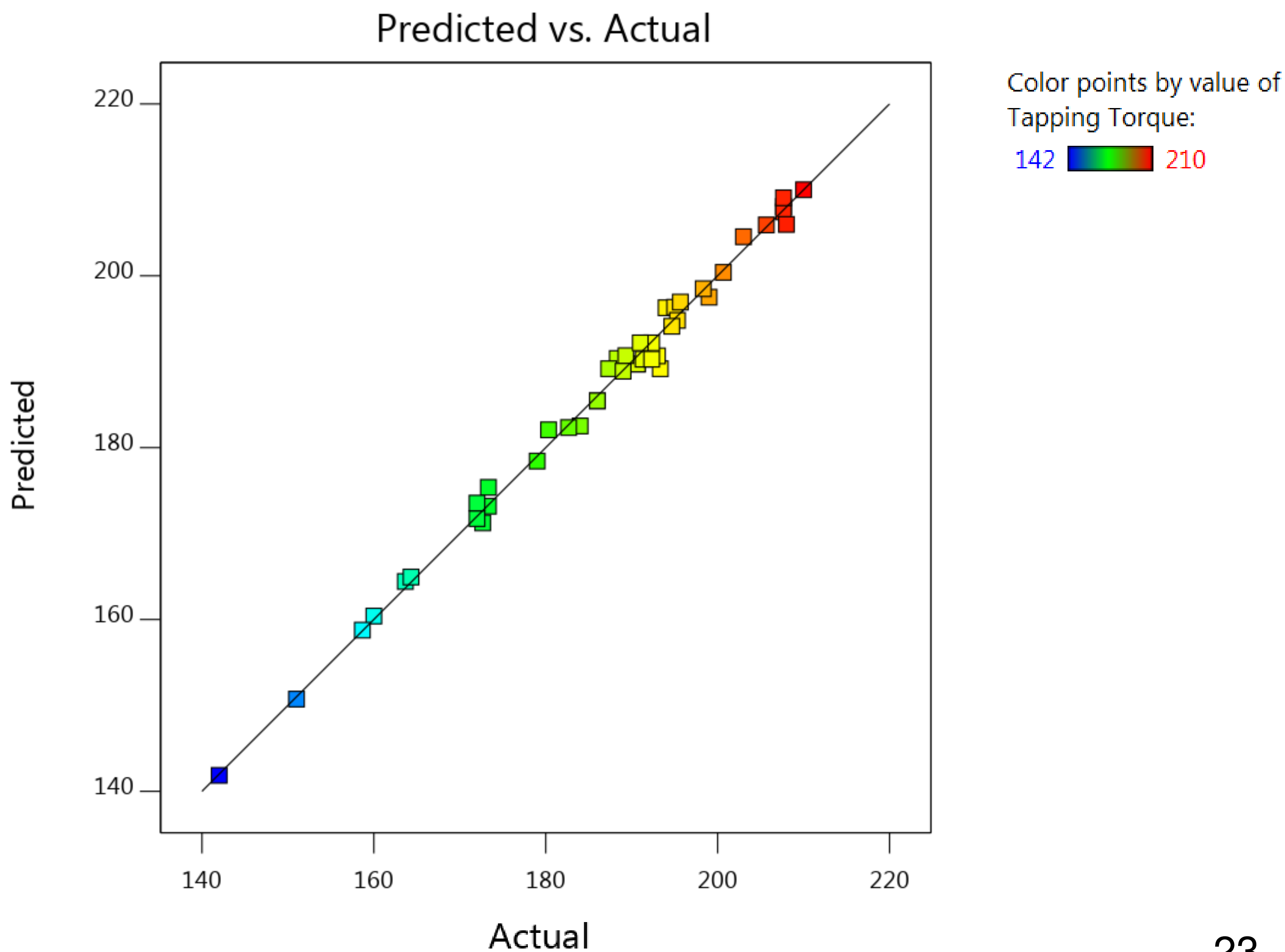
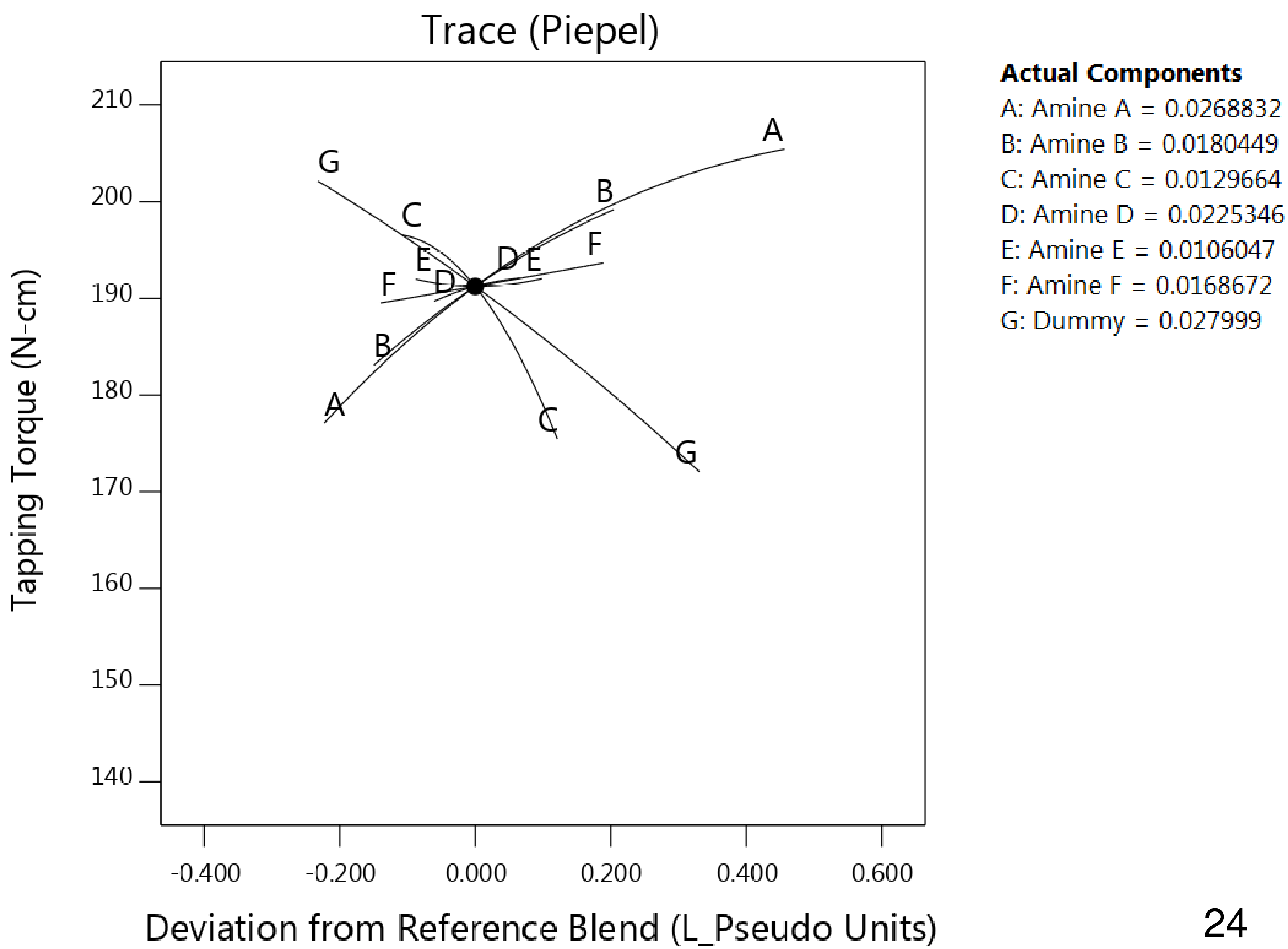


Trace Plot


Trace (Piepel)
Tapping Torque (N-cm)
210
200
190
180
170
160
150
140
-0.400
-0.200
0.000
0.200
0.400
0.600
Deviation from Reference Blend (L_Pseudo Units)
A
B
C
D
E
F
G
Actual Components
A: Amine A = 0.0268832
B: Amine B = 0.0180449
C: Amine C = 0.0129664
D: Amine D = 0.0225346
E: Amine E = 0.0106047
F: Amine F = 0.0168672
G: Dummy = 0.027999

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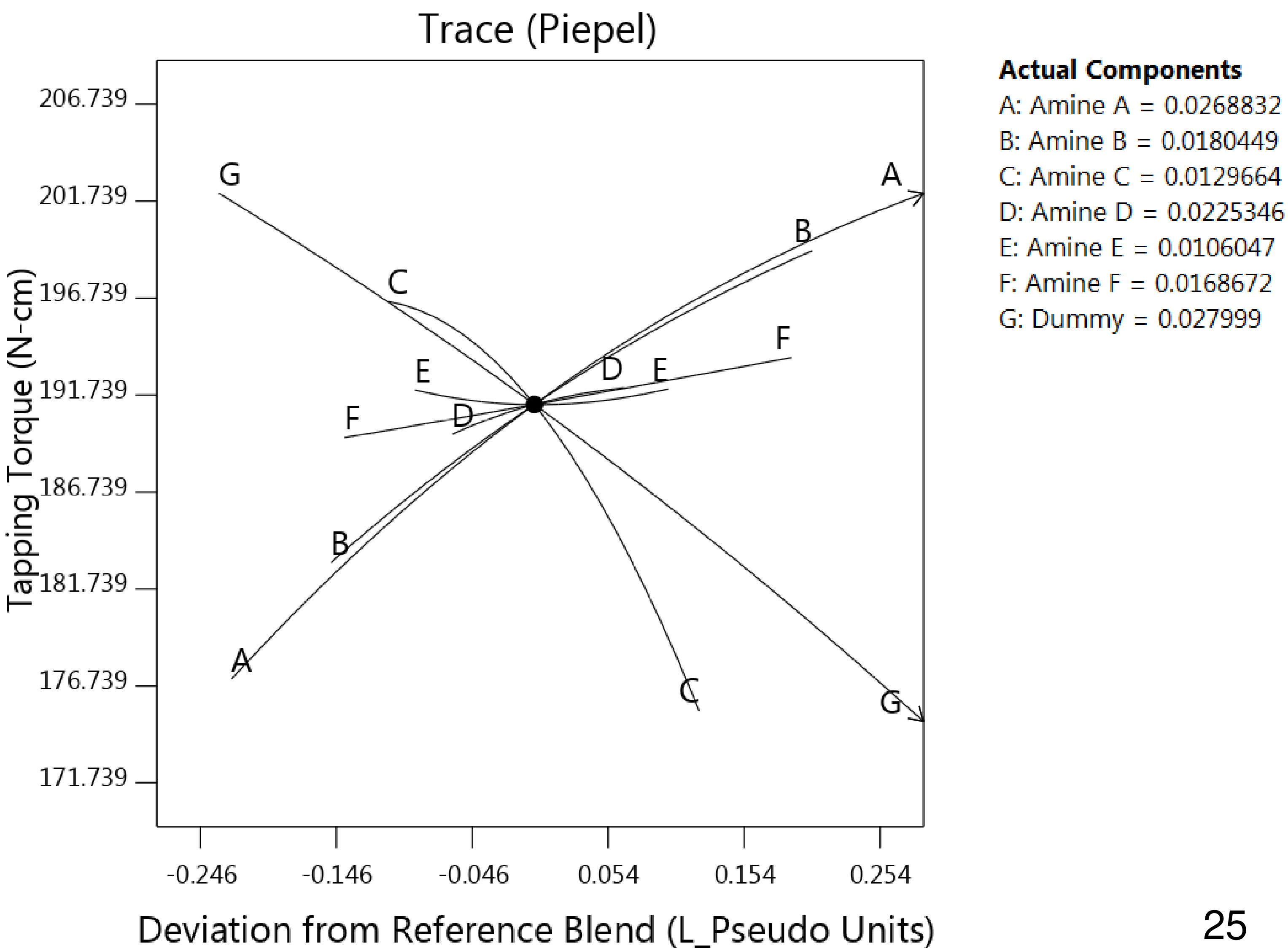

Trace (Piepel)
Tapping Torque (N-cm)
206.739
201.739
196.739
191.739
186.739
181.739
176.739
171.739
Deviation from Reference Blend (L_Pseudo Units)
-0.246
-0.146
-0.046
0.054
0.154
0.254
A
B
C
D
E
F
G
Actual Components
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Optimizing the Formulation

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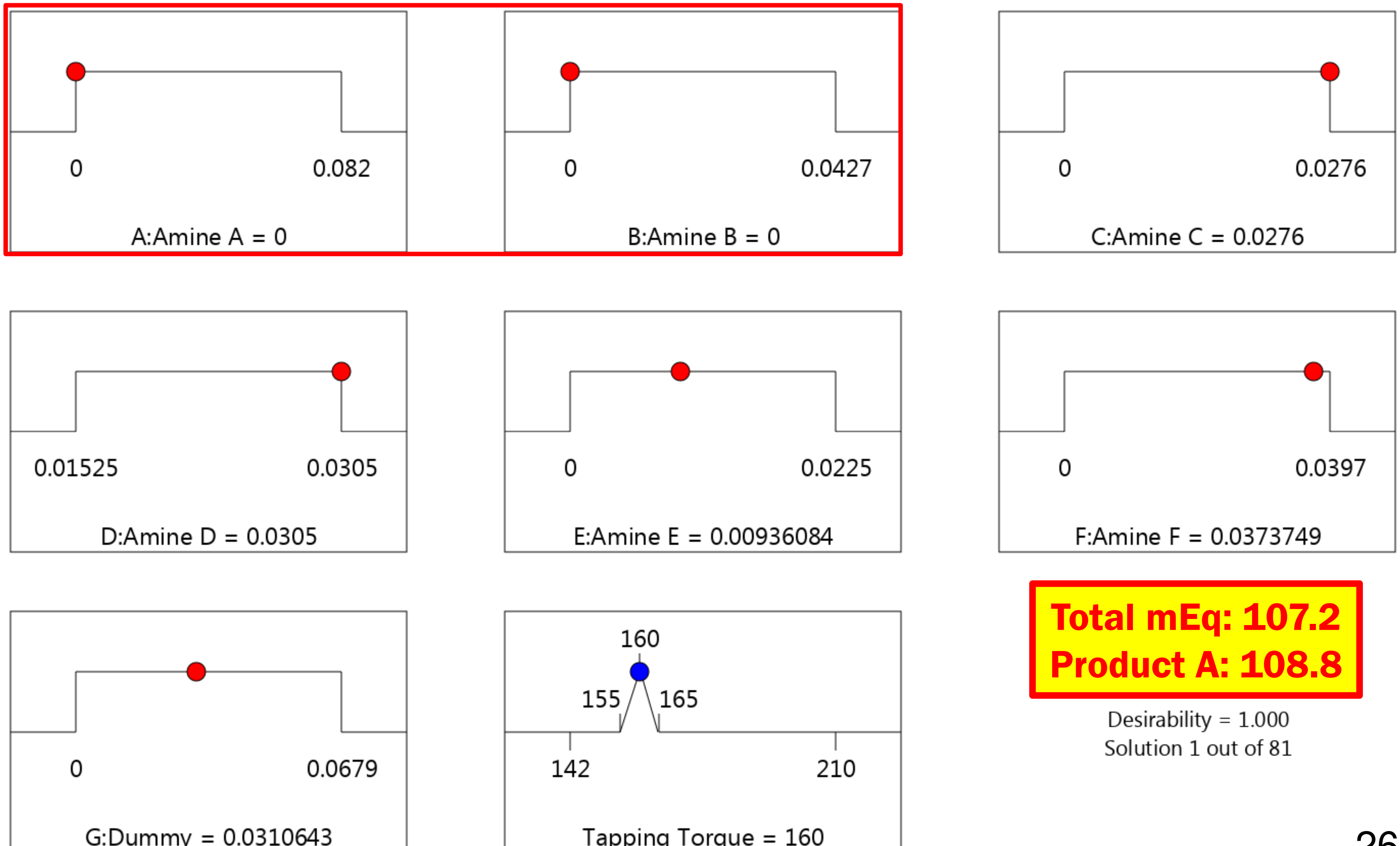
Optimal formulations, no component constraints:



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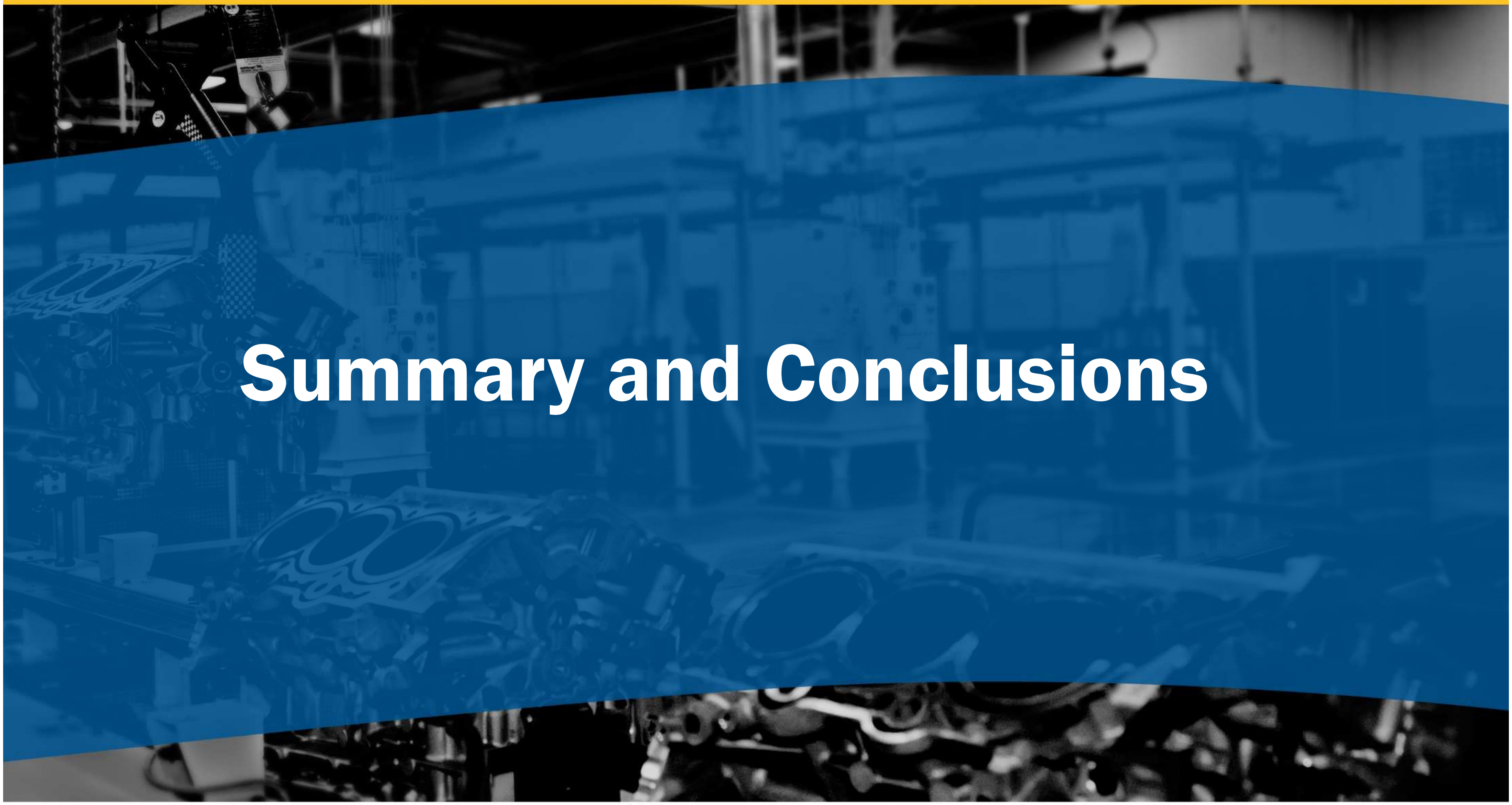
Summary and Conclusions



Summary

- Major takeaways from the investigation:
  - ***Amines are playing a major role in MWF lubrication***
  - ***The total amount of amine is almost as important as the choice of amines***
- Experimental design was able to determine the source of the performance issue
- We can use experimental design and Design-Expert® to analyze and optimize amine packages
- This information is being applied to other MWF development projects
- Experimental design has a place at Quaker!

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Thank you!

For questions or comments:
Jason Pandolfo
pandolfj@quakerchem.com
610-832-7819