Chlorinated Paraffin Replacement Challenges and Additive Selection Strategies

ILMA

6th International Metalworking Fluids Conference

January 8-10, 2024

T. McClure, A. Morgan: Sea-Land Chemical Co. - SLC Testing Services

INDUSTRY TRENDS DRIVING CHANGE IN MWF

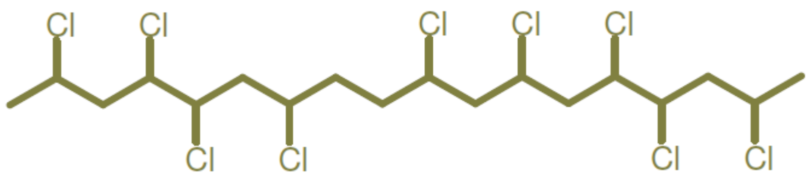
- Accelerating Advancements in Manufacturing and Materials Technologies
  - Vehicle Electrification
  - Vehicle and aerospace lightweighting:
    - AHSS (https://ahssinsights.org/) aluminum, magnesium, titanium, nickel alloys, SS, copper
  - Health, Safety, and Environmental Considerations: Sustainability
    - Global registrations, labeling, CPs, secondary amines, phosphorus bearing adds
  - Global Competition: Increasing Productivity
      - Higher speeds: Heat, foam,
      - Multimetal MWF
      - Less downtime: longer life fluids
      - Cost reduction
      - Speed to market

NEEDED TO SUPPORT CHANGES NEEDED IN MWF

Systematic, efficient, MWF formulation techniques, used along with rapid, flexible test methods which are predictive of field performance.

Friction and wear testing for CP replacement work

CHLORINATED PARAFFINS



- Chlorinated Aliphatic Hydrocarbons
  - Complex mixtures:
    - Chlorination of paraffin petroleum fractions and olefins
  - Characterized by carbon chain length of feedstock and % Chlorine
- Major Commercial Uses (since 1930s)
  - Lubricants: EP Additive
  - Plasticizer in plastics, coatings, adhesives, sealers, caulks and rubber
  - Flame retardant
  - Waterproof in textiles

CHLORINATED PARAFFIN LIMITATIONS

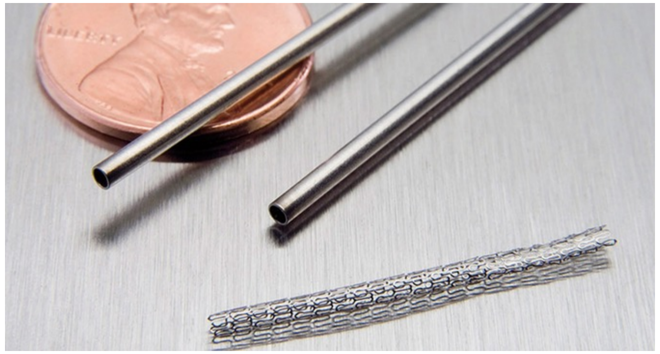
- Regulatory / HS&E Pressures
  - Regulations vary geographically
  - Global CP containing MWF formulations more difficult
- Ferrous Metal Stain and Corrosion:
  - Welding through residues on parts releases additional chlorides
- Removal Difficulties in Some Formulations / Applications
- Increased Fluid Disposal Costs
- Limited Solubility in Some Basestocks

WHY ARE CHLORINATED PARAFFINS STILL USED IN MWF?

- Highly Cost-effective E.P. additives:
  - Reactive EP plus polar film forming: Prevent Adhesive Failures
- Little Adverse Effects When Used at High Concentrations
  - Required for very severe MWF applications
    - Fineblanking, extrusion, deep drawing, tube drawing
    - Difficult to machine and form materials
- Versatility:
  - Oil soluble and easily emulsifiable
  - Perform well on a variety of metals
  - Compatible with common tool materials
  - Compatible with other common additives
  - Stability: biological and alkalinity
- Light color – low odor

TUBE APPLICATIONS REQUIRING CHLORINATED PARAFFINS

- Difficult to Work Materials
  - Austenitic stainless steels (300 series, 17-7PH), hastelloy, waspaloy, Inconel 625 and 718.
    - Tubing under 4mm diameter
    - Shaped tubing
    - Short run tube production



- Specific applications
  - Hypodermic syringe needles (<4mm)
  - LC/GC columns (<4mm)
  - Bourdon tubes (<4mm, elliptical)
  - Stents (<4mm)
  - Missile thrust chamber jackets (<4mm, shaped)
  - Nuclear control rods (<4mm)

TRIBOTESTING: BENCH AND SIMULATION TESTS

- Simulation Tests
  - Scaled down industrial process in laboratory
  - Use: Study influence of variables on production
  - Correlates well with production

- Bench Tests
  - Create specific tribological condition(s)
  - Use: Understand basic phenomena
  - Lower time and cost to run than simulation

- If mechanisms are understood:
  - May apply bench test results to production
  - May apply simulation test results to understanding basic phenomena

Schey, J. A. (1997), *A Critical Review of the Applicability of Tribotesters to Sheet Metalworking*, SAE 970714

SYSTEMATIC TRIBOTEST SELECTION: USING TRIBOSYSTEM ANALYSIS

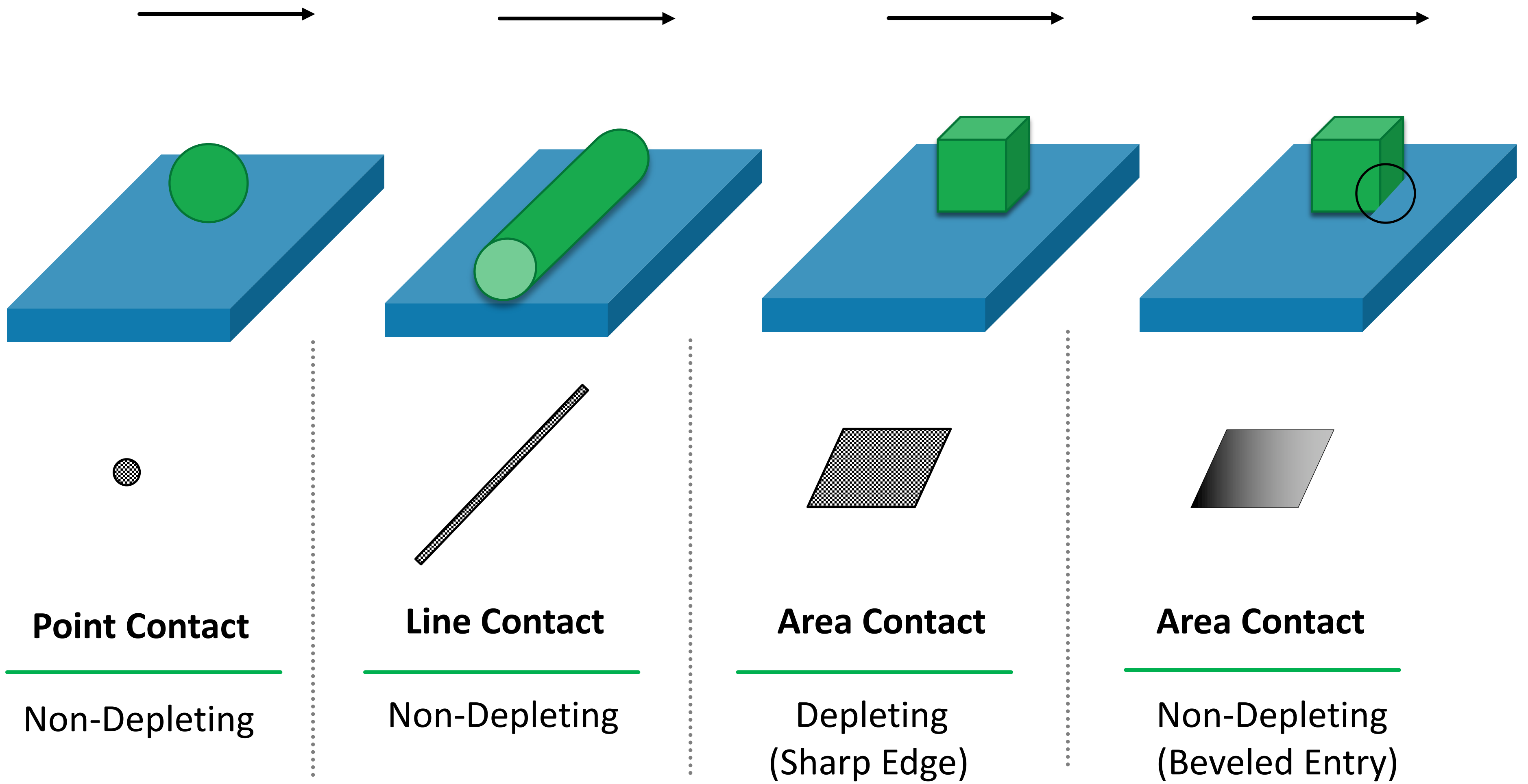
- Define the tribosystem for the actual production operation
- Define the tribosystem for the tribotests being considered
- Match the most important features of the MW operation with those of the tribotest(s)
- Run the tests and analyze results
- Validate test method(s) selected in the actual MW operation

Tribosystem Analysis Format

Section	Content
Heading	Project ID and Date: Short statement of problem
1	Hardware Configuration and Materials (surfaces)
1.1	Interface Descriptions
	Contact geometry, dimensions, arrangement, surface treatments, sketches, diagrams and photos.
2	Operating Environment
	Motion, loading, environment
3	Problem Description
	Failure mode: Damage (wear) type, performance metrics, constraints, history
4	Attachments and exhibits
	Additional data that may bear on the problem

Blau, Peter J. (2015), *Tribosystem Analysis: A Practical Approach to the Diagnosis of Wear Problems,* CRC Press, Taylor and Francis Group, Boca Raton, FL

TRIBOTEST CONTACT GEOMETRY: LUBRICANT DEPLETION



Gregory Dalton, P.Eng, PhD, College of the North Atlantic Faculty, TribSys Inc.

COMMON MWF TRIBOTEST SUMMARY

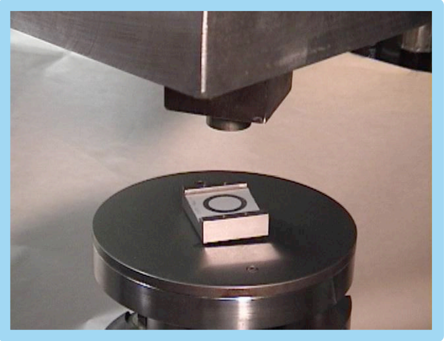
Test Method	Failure Mode(s)	Simulation / Bench	Contact	Depleting?	Lubrication Regime	Adhesion?	Wear Test?	COF Measured?
Four Ball EP	Adhesion / Galling	Bench	Point	N	EP, B	Y	Y	Y
Four Ball Wear	Tool wear	Bench	Point	N	B, Mixed, EHD	N	Y	Y
Pin and Vee Block- EP	Adhesion / Galling	Bench	Line	N	EP, B	Y	N	N
Pin and Vee Block- Wear	Tool wear	Bench	Line	N	B, Mixed	N	Y	N
Reichert and Brugger	Tool wear	Bench	Point	N	B, Mixed, EHD	N	Y	N
Tapping Torque (Roll form tap)	Tool wear/Adhesion	Simulation	Line - Area	N	B, Mixed, EHD	Y	N	N
Twist Compression Test (TCT)	Adhesion / Galling	Bench	Area	Y	EP, B, Mixed	Y	N	Y

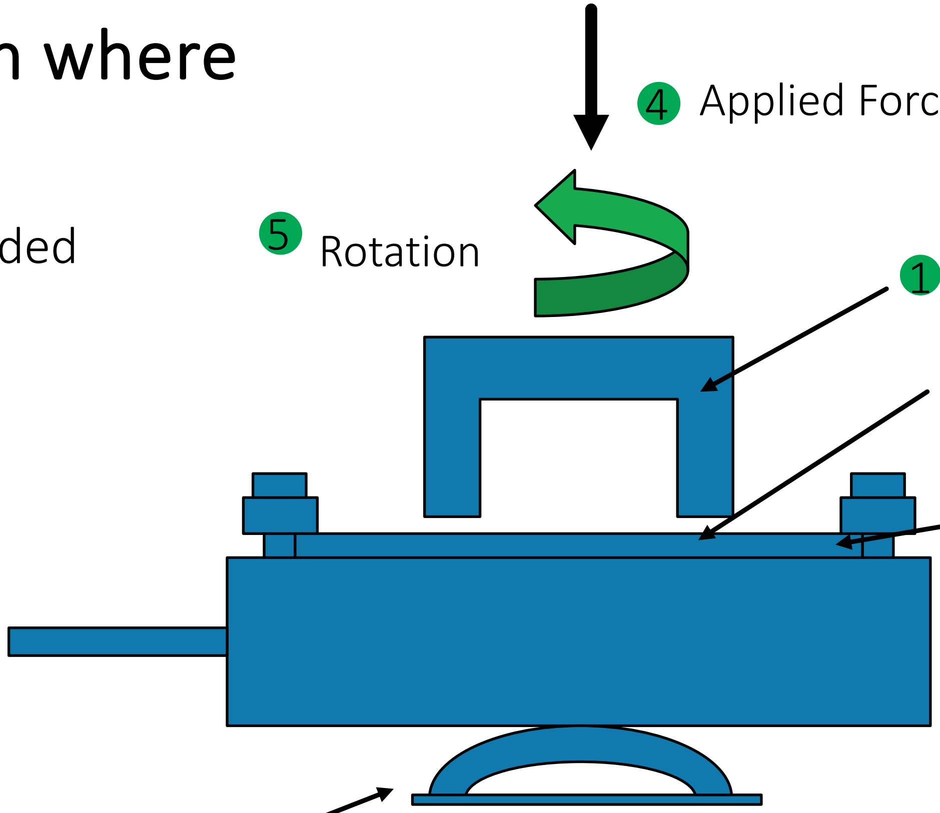
After: Schey, J. A. (1997), *A Critical Review of the Applicability of Tribotesters to Sheet Metalworking*, SAE 970714

TWIST COMPRESSION TEST: ASTM G223-23

- Contact creates boundary/lubricant starvation condition: Exists often where MWF failures occur

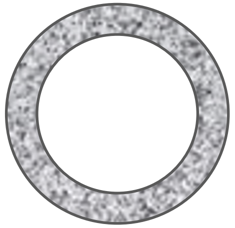
- Normal force and transmitted torque are recorded
- Speed is typically 10rpm (12mm/s)
- Interface pressure range: 7-276MPa (1-40ksi)
- Annulus: 25mm od X 19mm id





COF = T/N

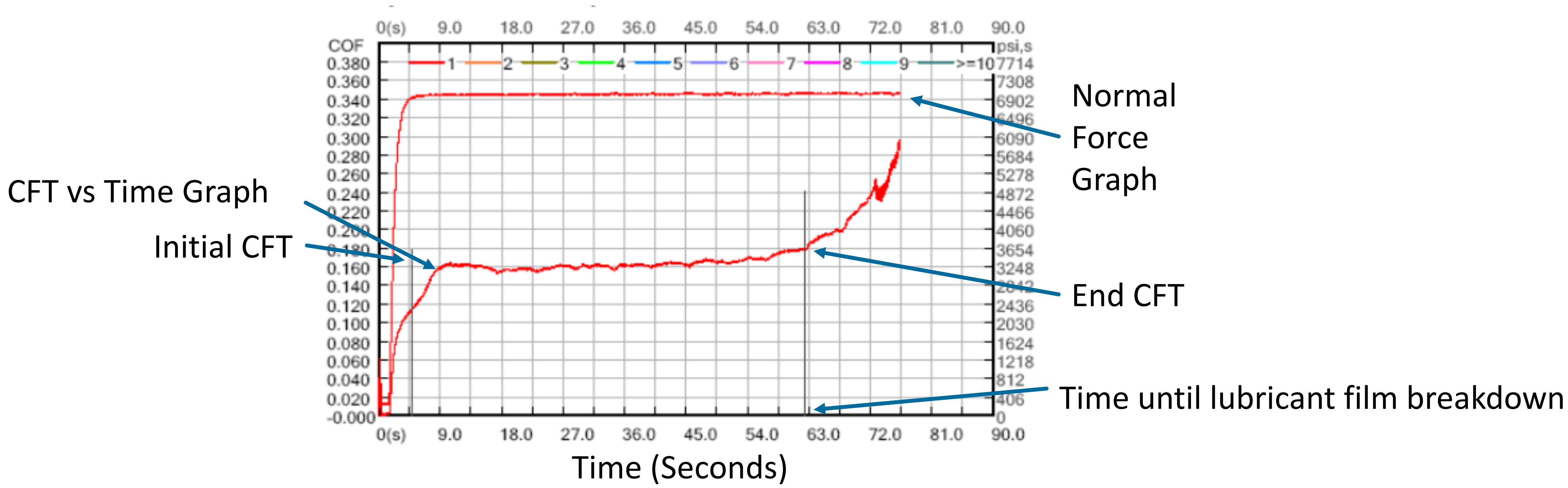
where N is the Normal force
T is the transmitted torsional force



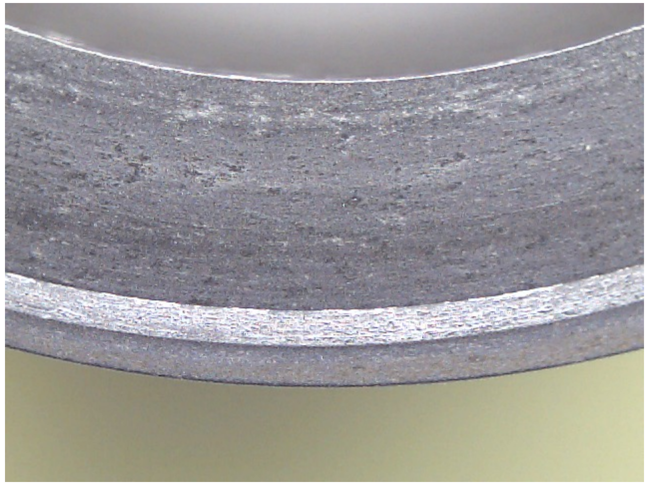
Contact Pattern
(Squeeze-film)

TCT TEST RESULTS: ASTM G223-23

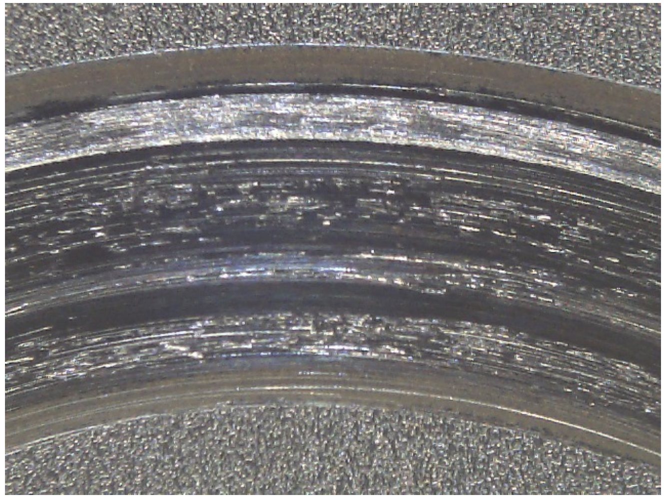
- Initial Coefficient of friction in TCT (CFTi)
- Time until lubricant film failure (TBD)
- Average coefficient of friction (CFT Avg)
- Avg CFT after a specific time: 30 seconds
- Coefficient of friction at specific time: 5 seconds
- Friction Factor: TBD/(0.2CFTi+0.8CFTavg)
- Surface damage/galling
- Tribochemical residue analysis



MATCHING FAILURE MODE OF PRODUCTION WITH TRIBOTEST (TCT)



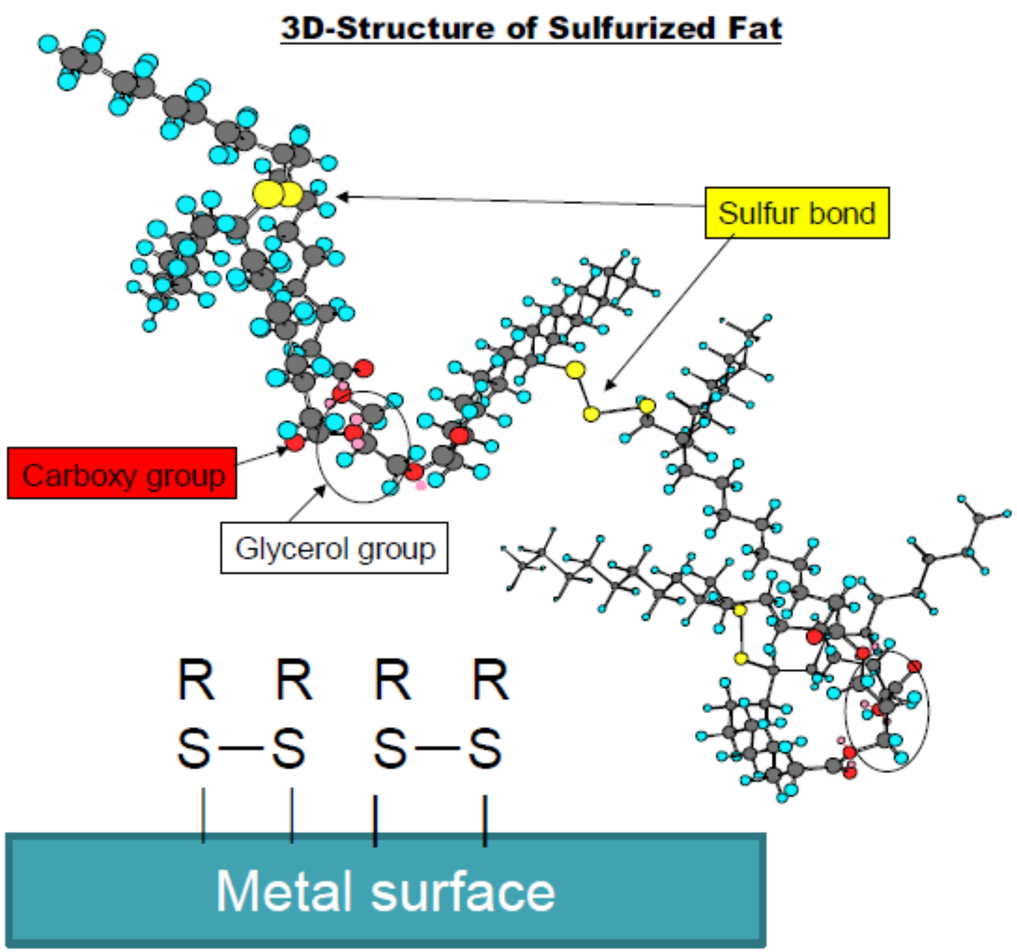
TCT D2 Tool Steel



TCT 1008 CRS Sheet

CHLORINATED PARAFFIN REPLACEMENTS: SULFURIZED

- Consists of Sulfur Chain and Carrier (EP + Polar film formers)
  - Vary both to tailor properties / performance
    - Olefins (20-40% S)
    - Triglycerides (10-20% S)
    - Esters (10-30% S)
    - Fatty acids (~10% S)
- Dark color – high odor
- Light color – low odor

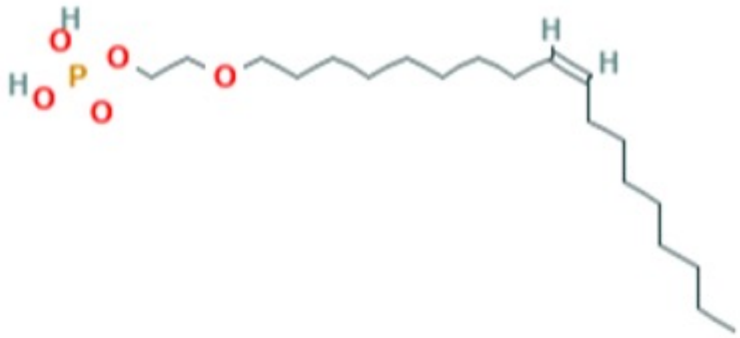


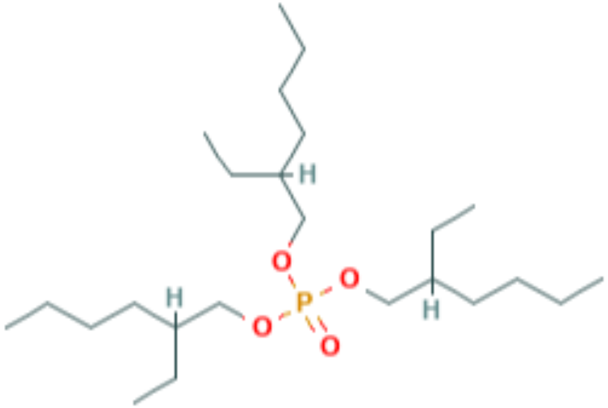
SULFURIZED E. P. ADDITIVE POTENTIAL LIMITATIONS

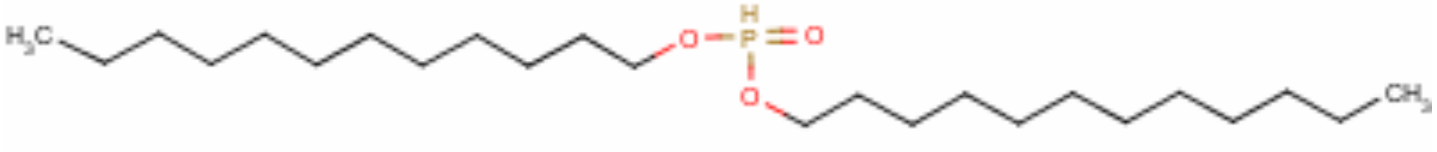
- Staining of copper alloys for active S grades
- High activity additives may attack some tool coatings
- High tool wear possible (tribocorrosion)
  - High activity sulfur at >4% S
- Increasing S content does not always increase load carrying capability
- Less activity than CP with some metals
- Enhanced biological activity
- Color and odor vary

CHLORINATED PARAFFIN REPLACEMENTS: PHOSPHORUS BEARING

- Phosphate Esters
  - Mono, di and tri esters
  - Length of carbon chains (C-6 to C-18
  - Degree of alkoxylation
  - Acid values (0->350mgKOH/g)
  - 1-14% Phosphorous content
  - Solubility: Water and most basestocks
- Phosphites
- ZDDP





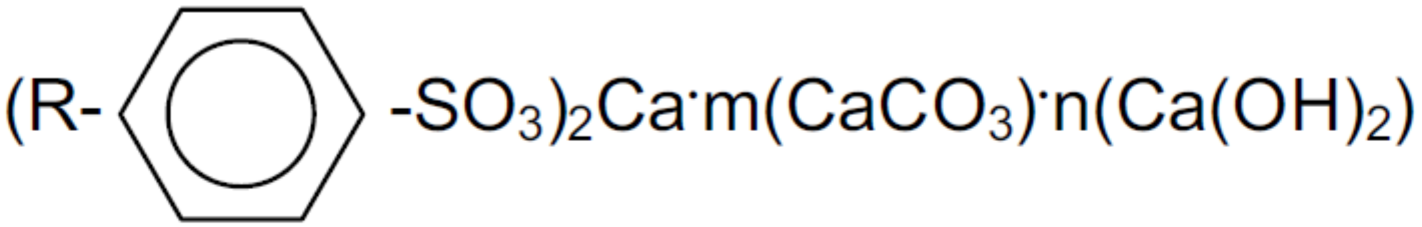


PHOSPHORUS BASED E. P. ADDITIVE POTENTIAL LIMITATIONS IN MWF

- Enhanced biological activity
- Potential regulatory pressure
  - Great lakes algal blooms
- Low P content (compared with Cl in CP)
- Limited benefit to using high levels
- Carbide cobalt leaching potential

CHLORINATED PARAFFIN REPLACEMENTS: OVERBASED SULFONATES

- Not a chemical reactive E.P.
  - Metal carbonate / hydroxide particles dispersed in oil with sulfonate (calcium, sodium or magnesium sulfonate)
- Various particle sizes
  - Crystalline – larger – gelled
  - Amorphous – colloidal
- Total base number (TBN) to 400mgKOH/g
- Synthetic or natural (petroleum) sulfonates



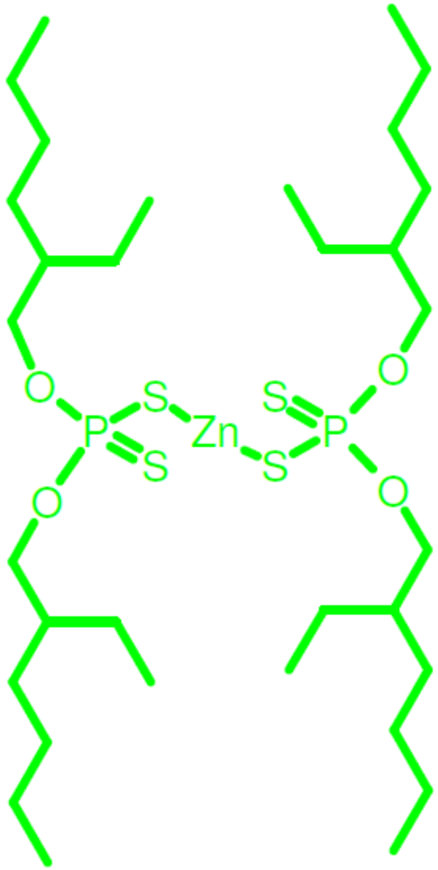
OVERBASED SULFONATES

- Advantages
  - Synergistic with Sulfur and Chlorine E.P.
  - Corrosion protection
  - Acid scavenging
  - Detergent

- Formulation Limitations:
  - Compatibility
    - Gelling in oils containing some fatty acids and esters
    - Acid phosphates and some active sulfur sources
  - Primarily used in straight oils

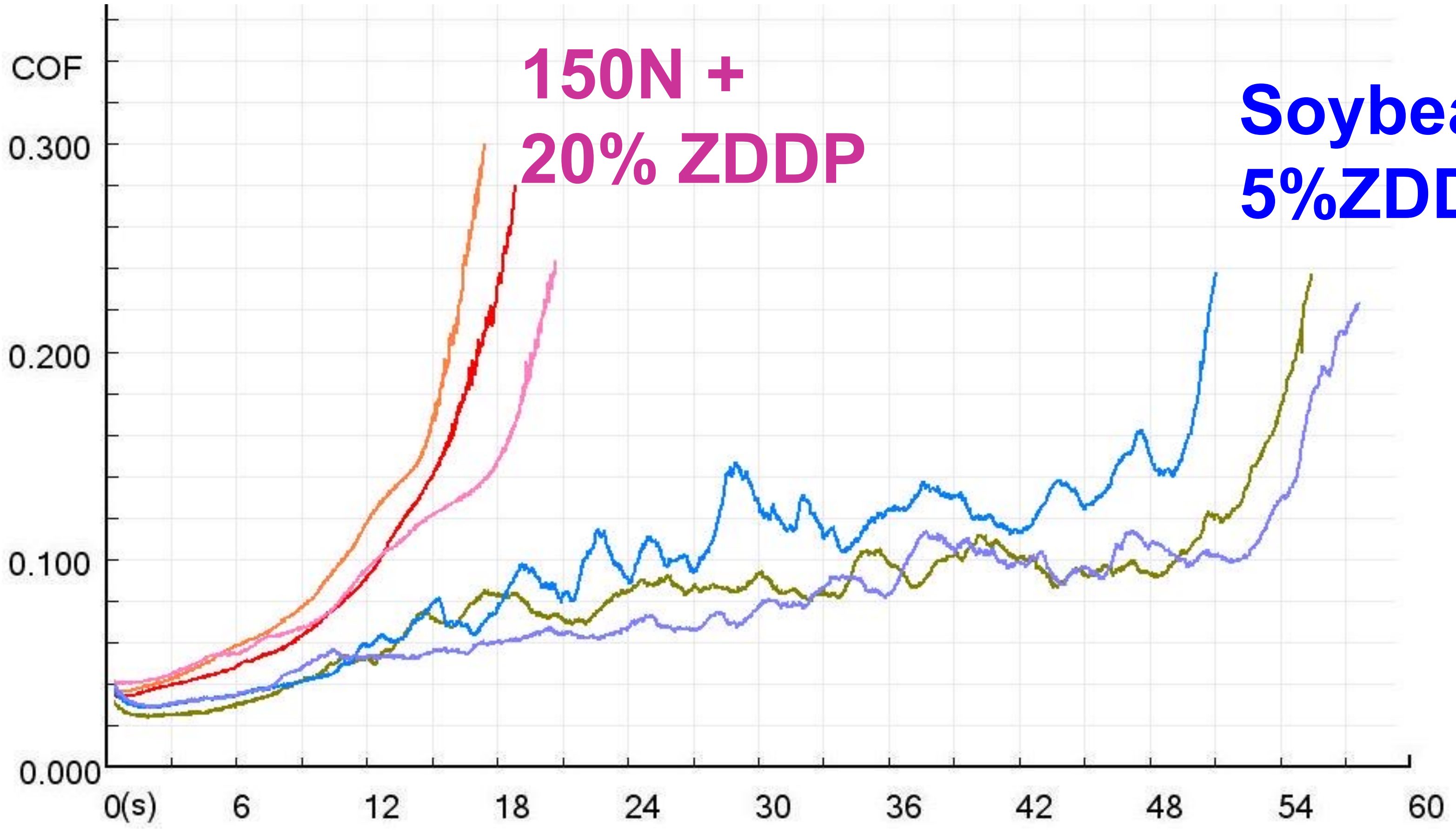
CHLORINATED PARAFFIN REPLACEMENTS

- Others
  - Zinc and Molybdenum compounds
  - Simple, complex and polymeric esters
  - Polyalkylene glycols (water soluble)
  - Polymers
  - Solid lubricants($CaCO_3$, graphite, MoS_2, nanoparticles)
  - Other fatty acids and fatty derivatives
- *Combinations of additives are required to replace chlorinated paraffins in many applications*



BASESTOCK SELECTION AND ADDITIVE RESPONSE

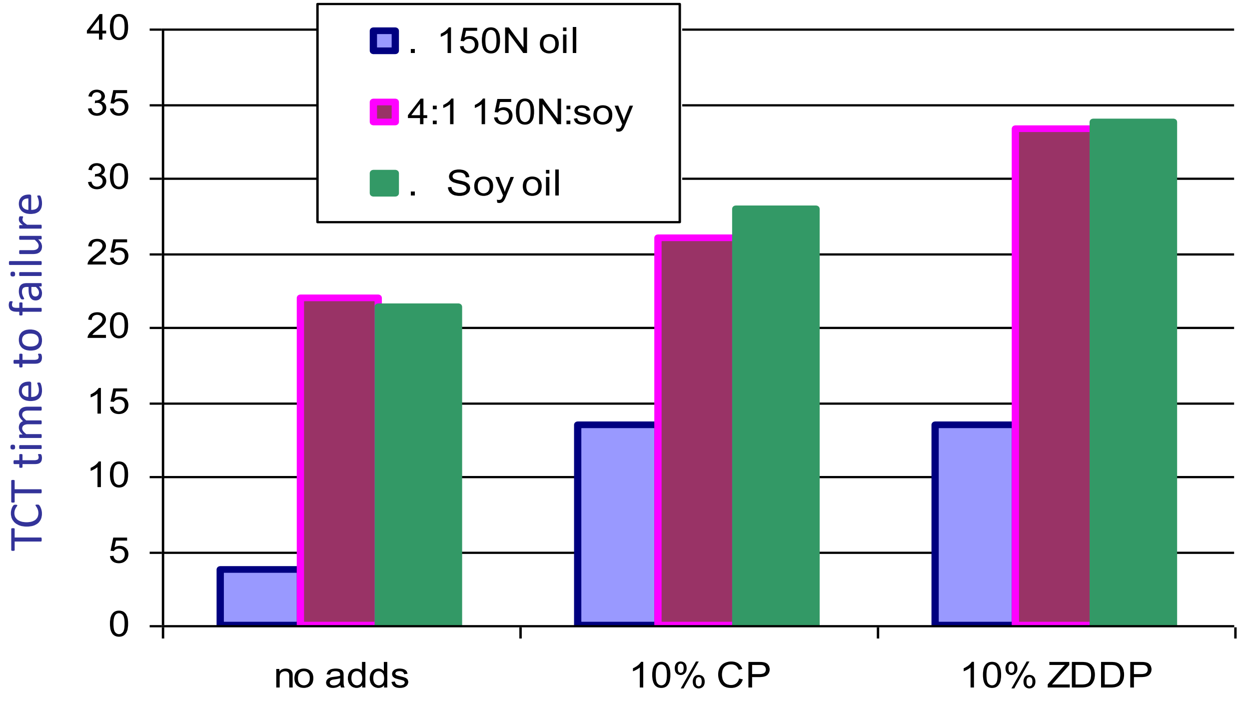
ZDDP Blends: 29ksi / SAE 1008 CRS: TCT COF vs Time Comparisons



Tribology Letters (2010) 37:111-121, S. J. Asadauskas, Girma Biresaw, T. McClure

Note: CP showed similar behavior

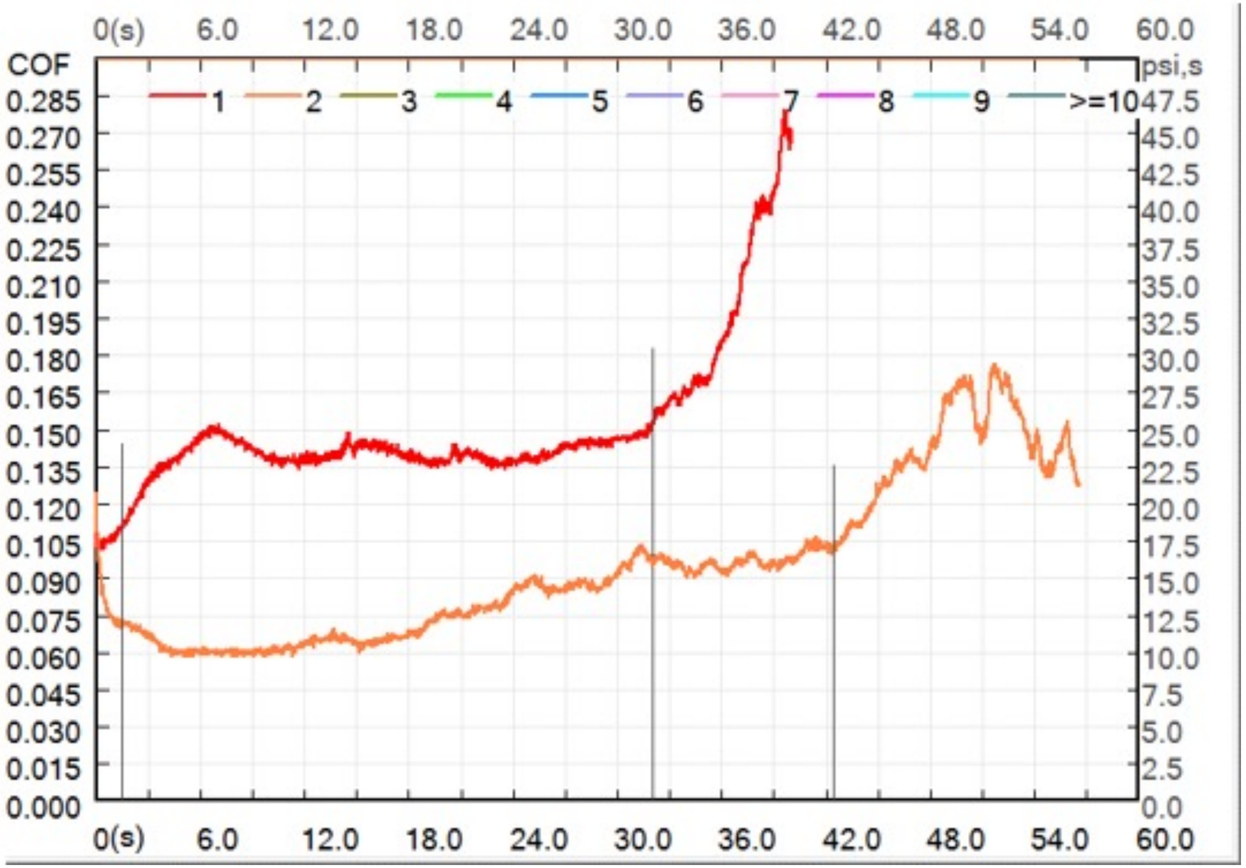
10% EP ADDITIVE RESPONSE (TCT TBD) IN BASESTOCK BLEND



20% SBO in 150N gave similar response to 100% SBO basestock

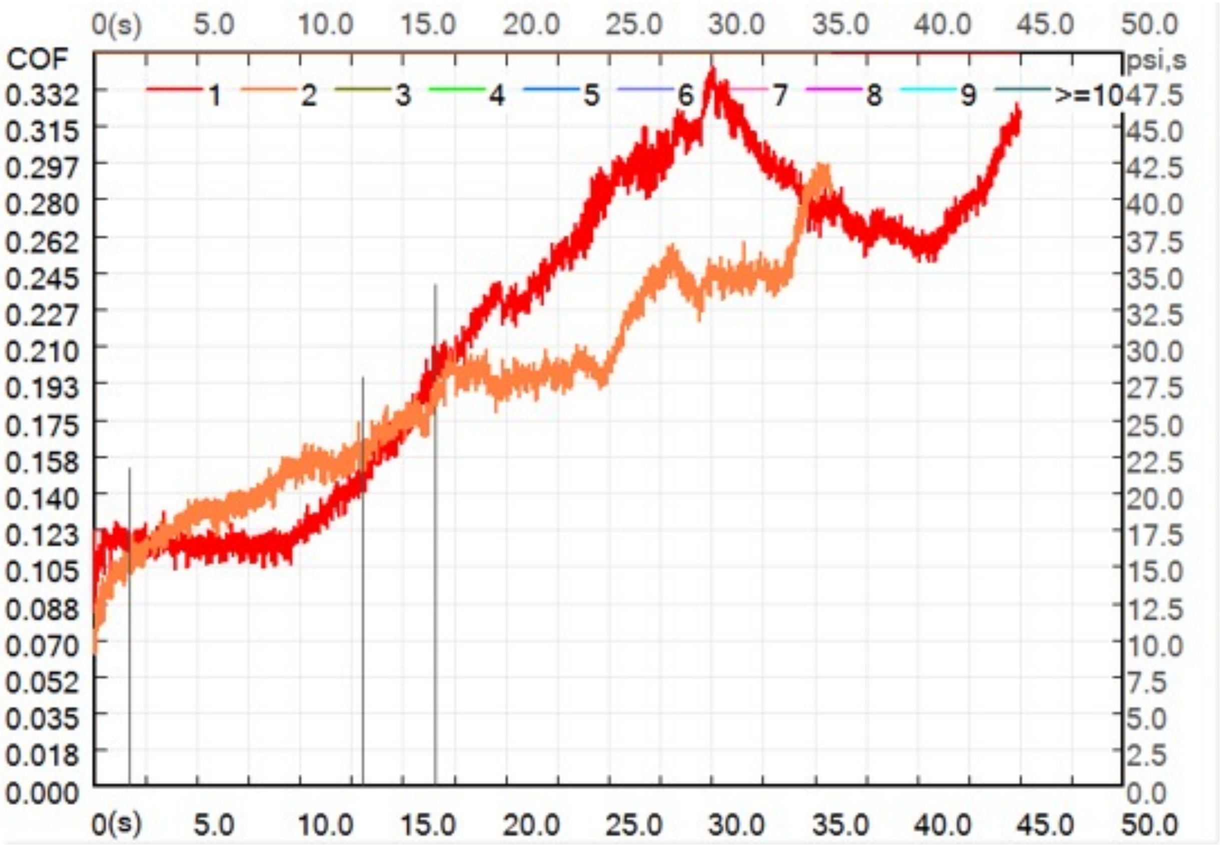
Tribology Letters (2010) 37:111-121, S. J. Asadauskas, Girma Biresaw, T. McClure

AISI 1008 CRS: 10% SULFURIZED OLEFIN IN NAPHTHENIC AND VEGETABLE OIL COMPARISON: TCT COF VS TIME GRAPHS: 15KSI



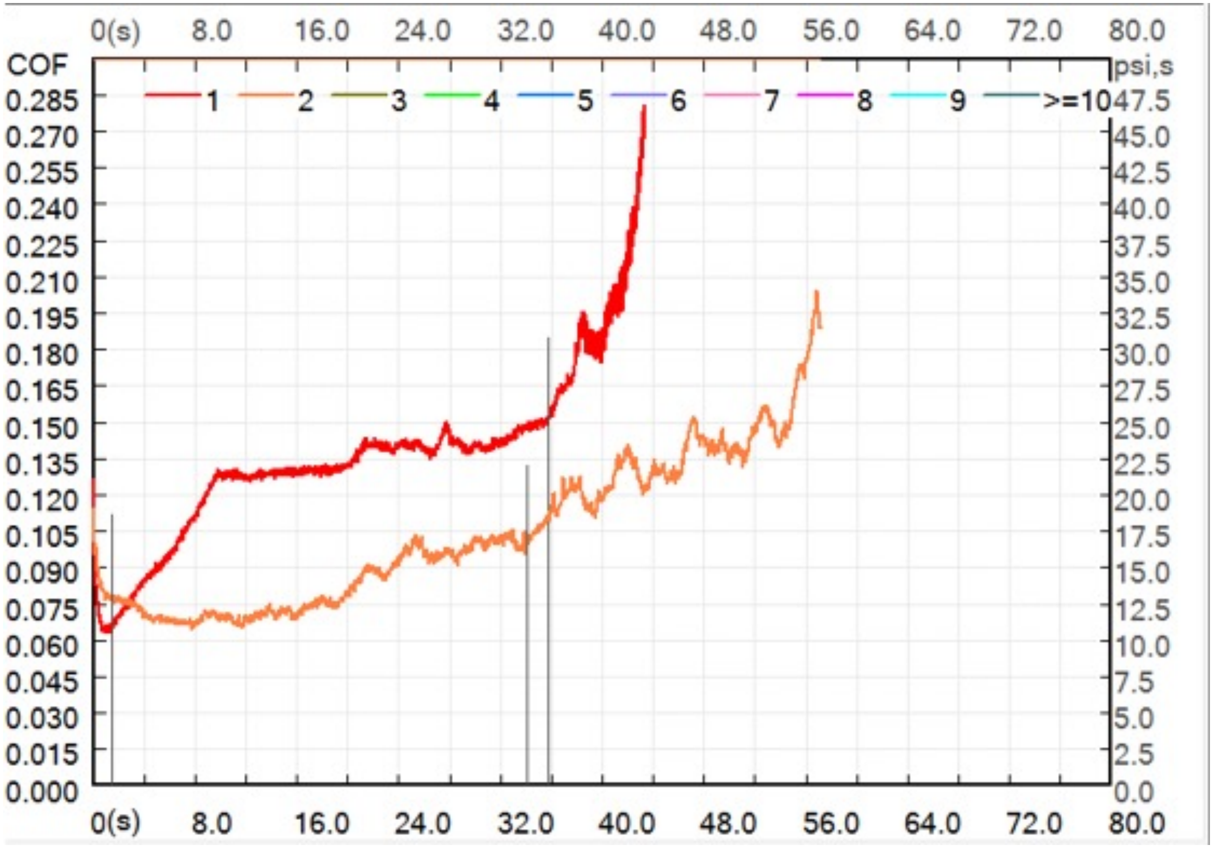
Lubricant	COFi	COFa	TBD	COF5	FF
Naphthenic	0.111	0.146	29.22	0.145	210
Vegetable	0.073	0.079	40.58	0.061	522

SS304: 10% SULFURIZED OLEFIN IN NAPHTHENIC AND VEGETABLE OIL COMPARISON: TCT COF VS TIME GRAPHS: 3KSI



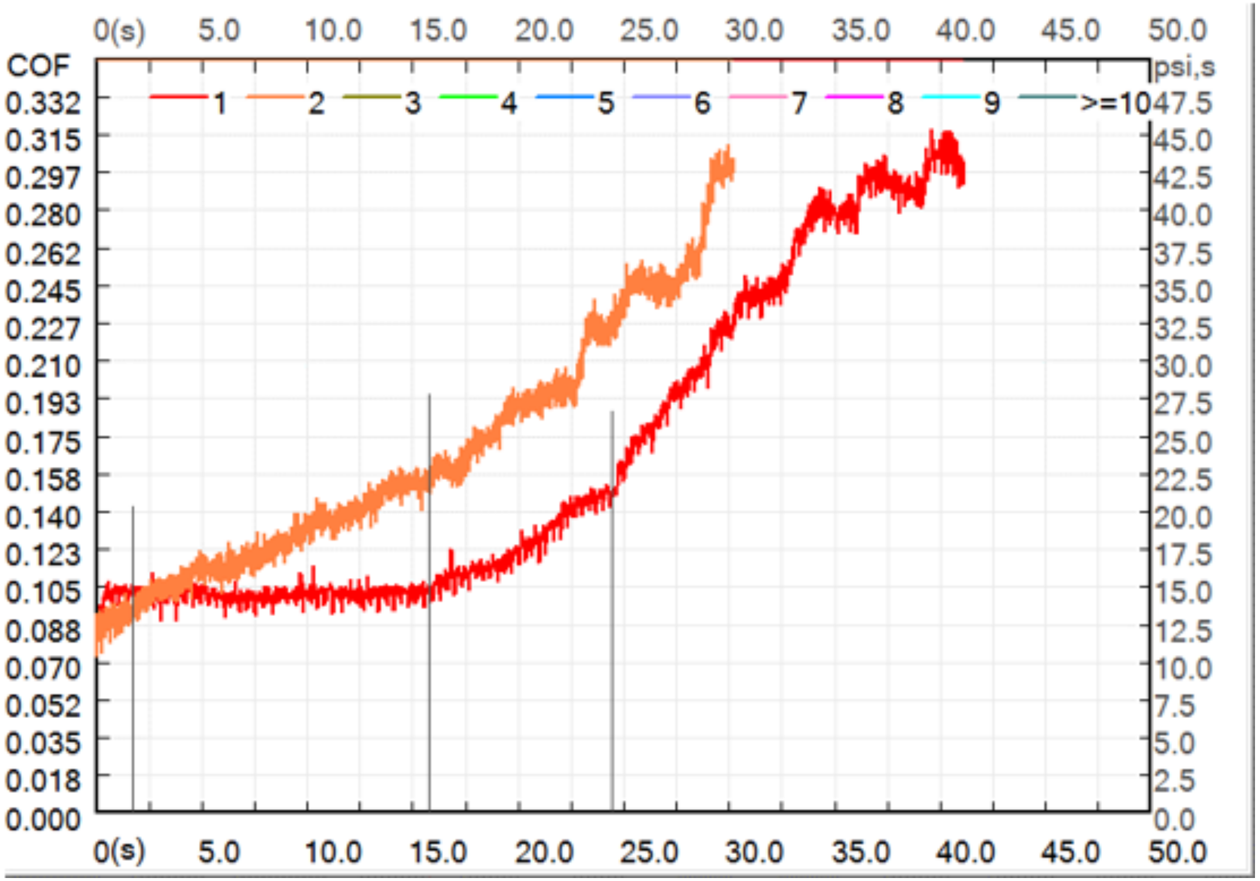
Lubricant	COFi	COFa	TBD	COF5	FF
Naphthenic	0.118	0.136	14.42	0.116	109
Vegetable	0.107	0.135	10.24	0.132	79

AISI 1008 CRS: 10% SULFURIZED OLEFIN+5% PHOSPHITE IN NAPHTHENIC AND VEGETABLE OIL COMPARISON: TCT COF VS TIME GRAPHS: 15KSI



Lubricant	COFi	COFa	TBD	COF5	FF
Naphthenic	0.073	0.131	33.06	0.106	277
Vegetable	0.078	0.079	31.09	0.067	395

SS304: 10% SULFURIZED OLEFIN+5% PHOSPHITE IN NAPHTHENIC AND VEGETABLE OIL COMPARISON: TCT COF VS TIME GRAPHS: 3KSI



Lubricant	COFi	COFa	TBD	COF5	FF
Naphthenic	0.102	0.110	20.63	0.100	190
Vegetable	0.096	0.125	13.49	0.118	113

WORKPIECE MATERIAL CONSIDERATIONS

- Which workpiece alloys are most likely to be involved in "critical uses" for CPs?
- Are partial CP substitutions effective?
- Does the inclusion of over 20% vegetable oil improve the performance of replacement packages when used with low levels of CP?

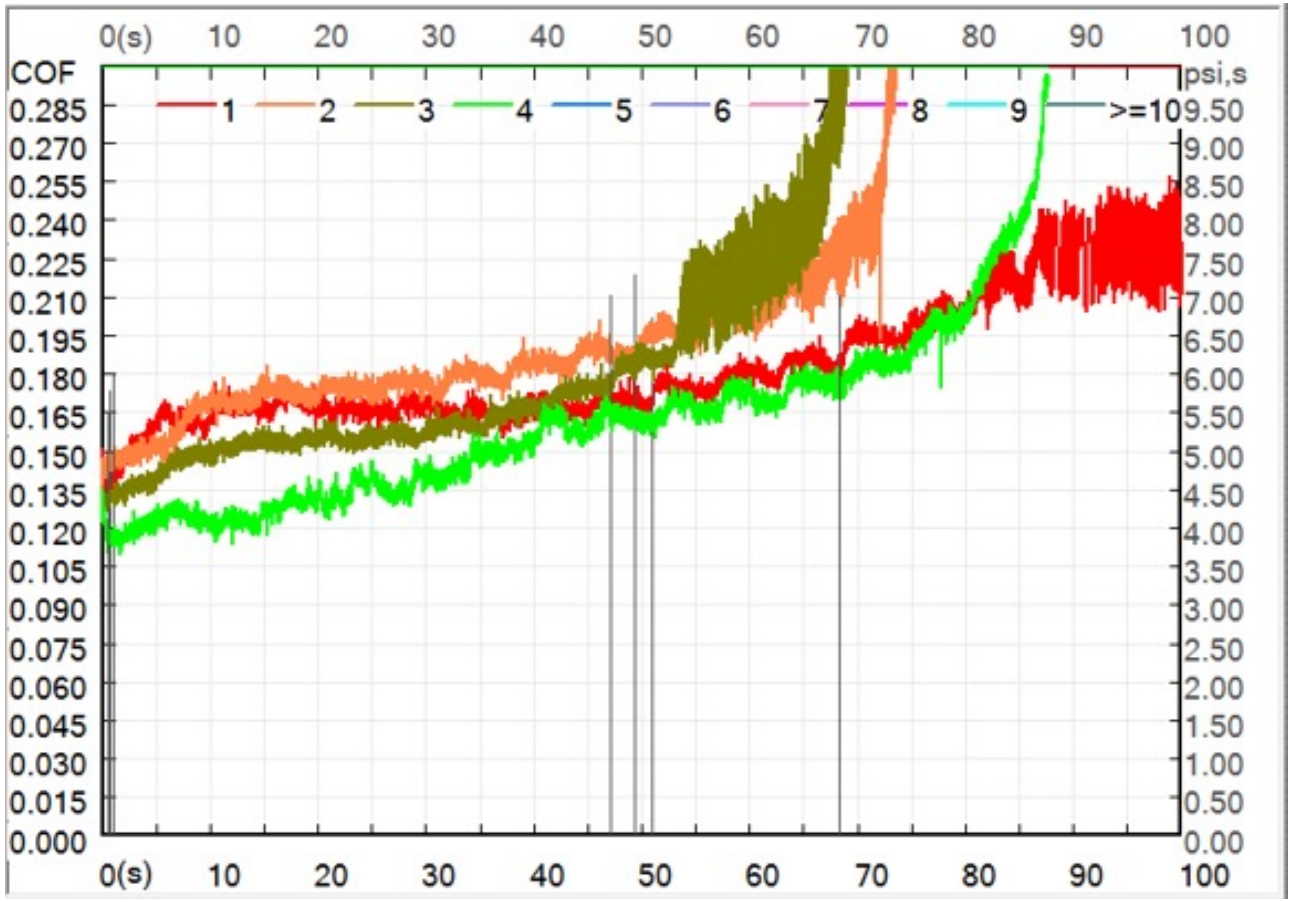
TEST FORMULAS (25CST. @ 40^{o}C)

Ingredient	CP10	A	ACP	ACP SBO
Naphthenic Basestock(s)	90.00	80.00	83.00	46.60
vLCCP (48%Cl)	10.00	0.00	3.00	3.00
Sulfurized olefin (37%S)	0.00	10.00	7.00	7.00
High Polarity Olefin Copolymer	0.00	5.00	3.50	3.50
ZDDP	0.00	5.00	3.50	3.50
Soybean Oil	0.00	0.00	0.00	36.40
Total	100.00	100.00	100.00	100.00

WORKPIECE MATERIALS

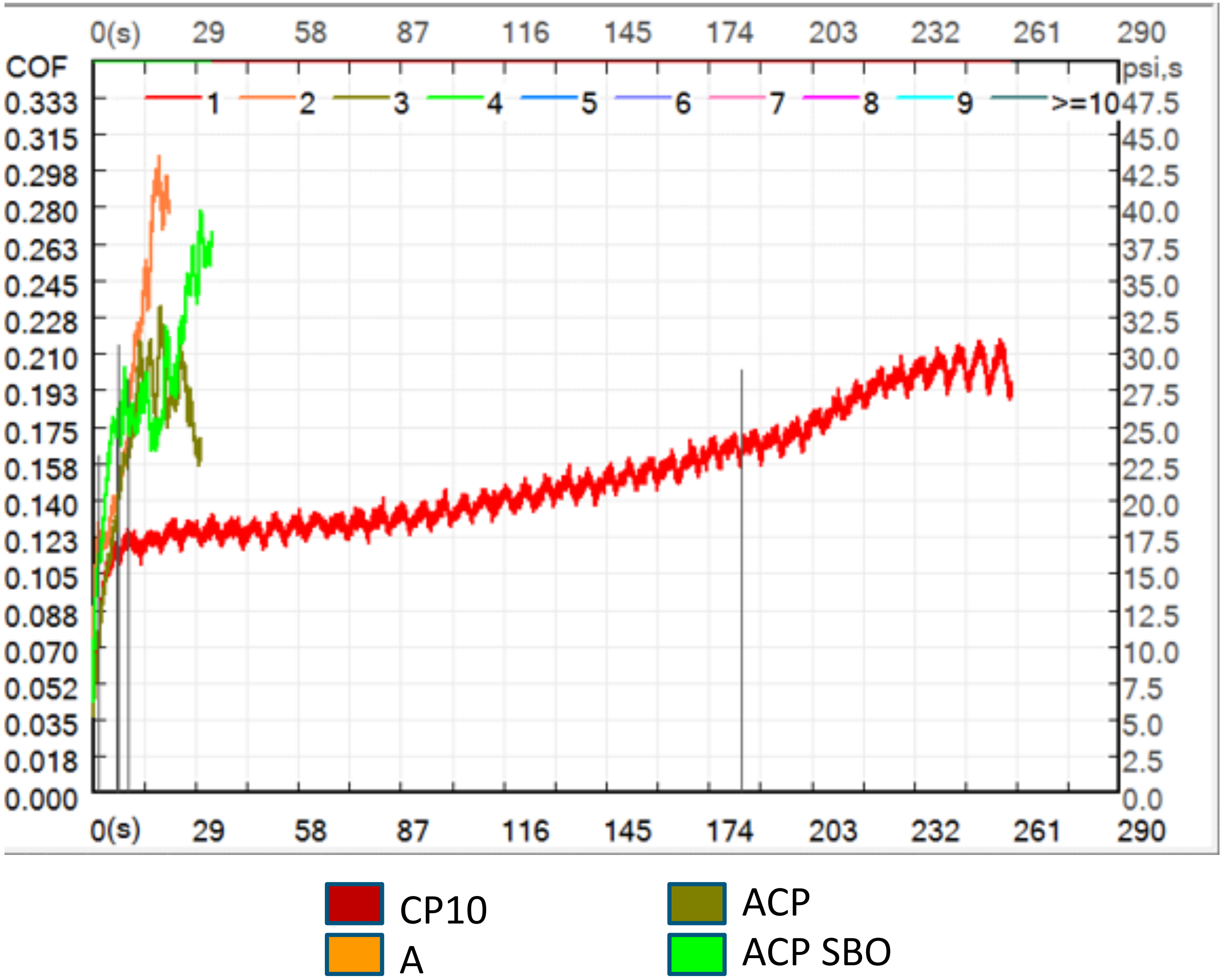
Metal	Type	YS(psi)	TS(psi)	Fe (approx.)	Ni	Cr	Ti	Co	Mo	Mn	Al	Other
CRS 1008	Mild Steel	25000	44000	99	NA	NA	NA	NA	NA	0.4	NA	NA
DP600	Dual Phase AHSS	87000	101500	98	NA	NA	NA	NA	NA	1.4	NA	NA
SS409	Ferritic	37460	62170	88	0.168	10.92	0.107	0.016	NA	0.406	NA	.25 Nb
SS410	Martensitic	46400	79000	87	0.25	12.29	NA	NA	0.05	0.54	0.001	NA
SS304	Austenitic	41035	94365	72	8.13	18.35	NA	NA	NA	1.03	NA	NA
A286	Fe Based Superalloy	50500	97000	56	24.82	14.52	2.13	0.06	1.19	0.3	0.16	NA
Inconel 718	Nickel Based	70000	122000	20	52.18	17.96	1.02	0.16	2.86	0.12	0.61	4.98 Cb
Waspaloy	Nickel Based High Cobalt	90000	150000	2	57	19.1	3.14	13.38	4.29	0.06	1.44	NA

AISI 1008 CRS: 5KSI TCT COF VS TIME GRAPHS

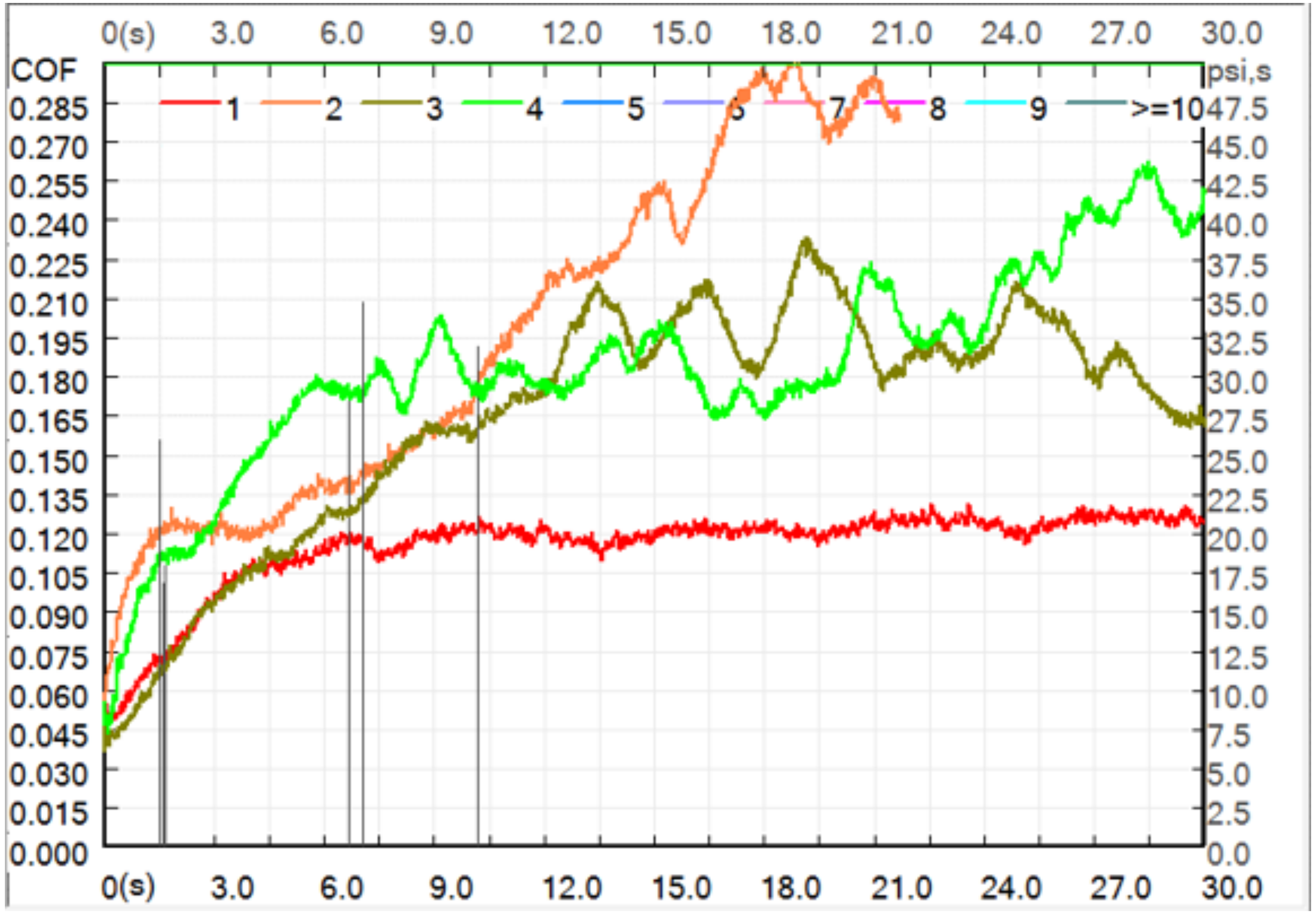


CP10
A
ACP
ACP SBO

SS304: 2KSI TCT COF VS TIME GRAPHS

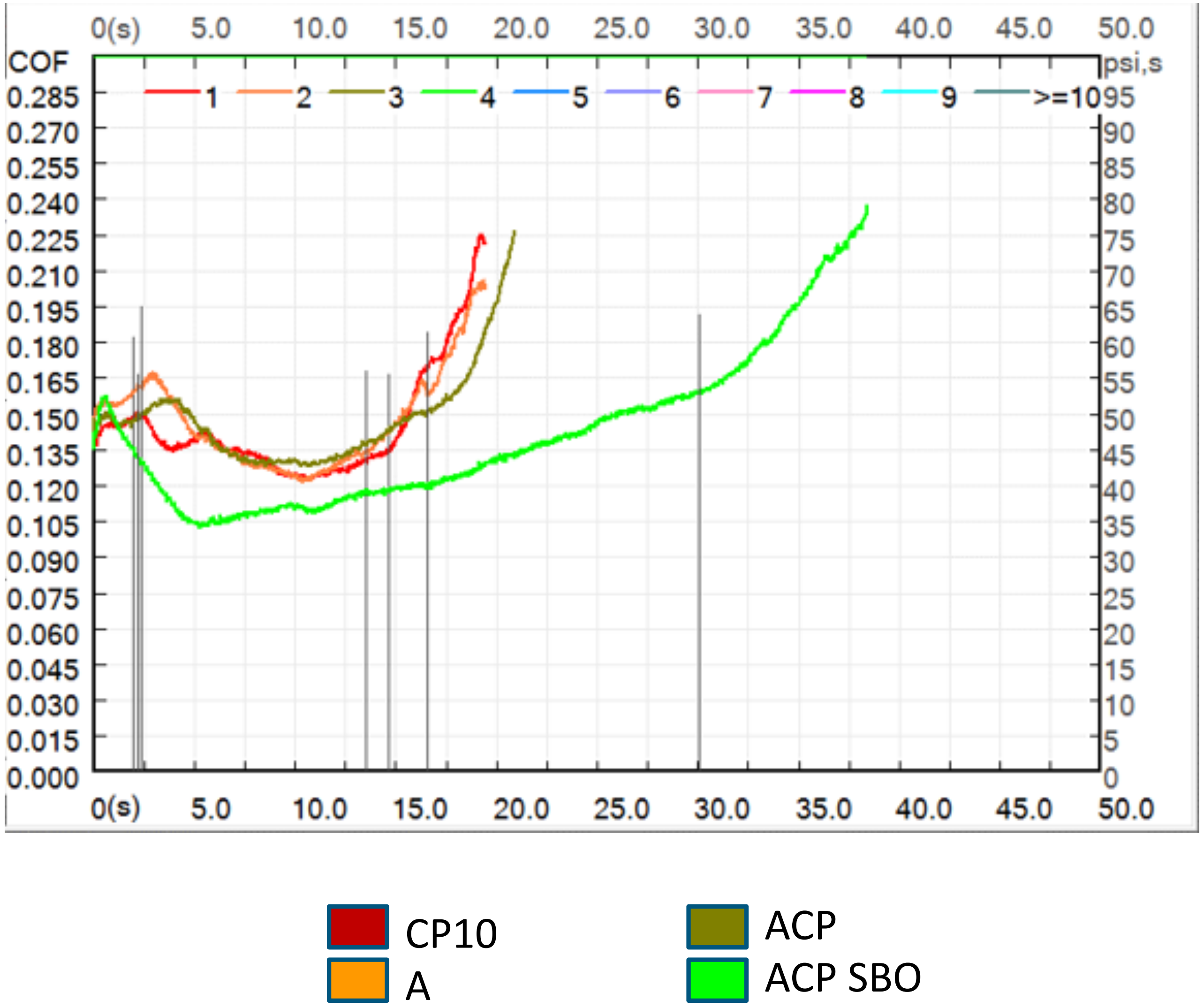


SS304: 2KSI TCT COF VS TIME GRAPHS

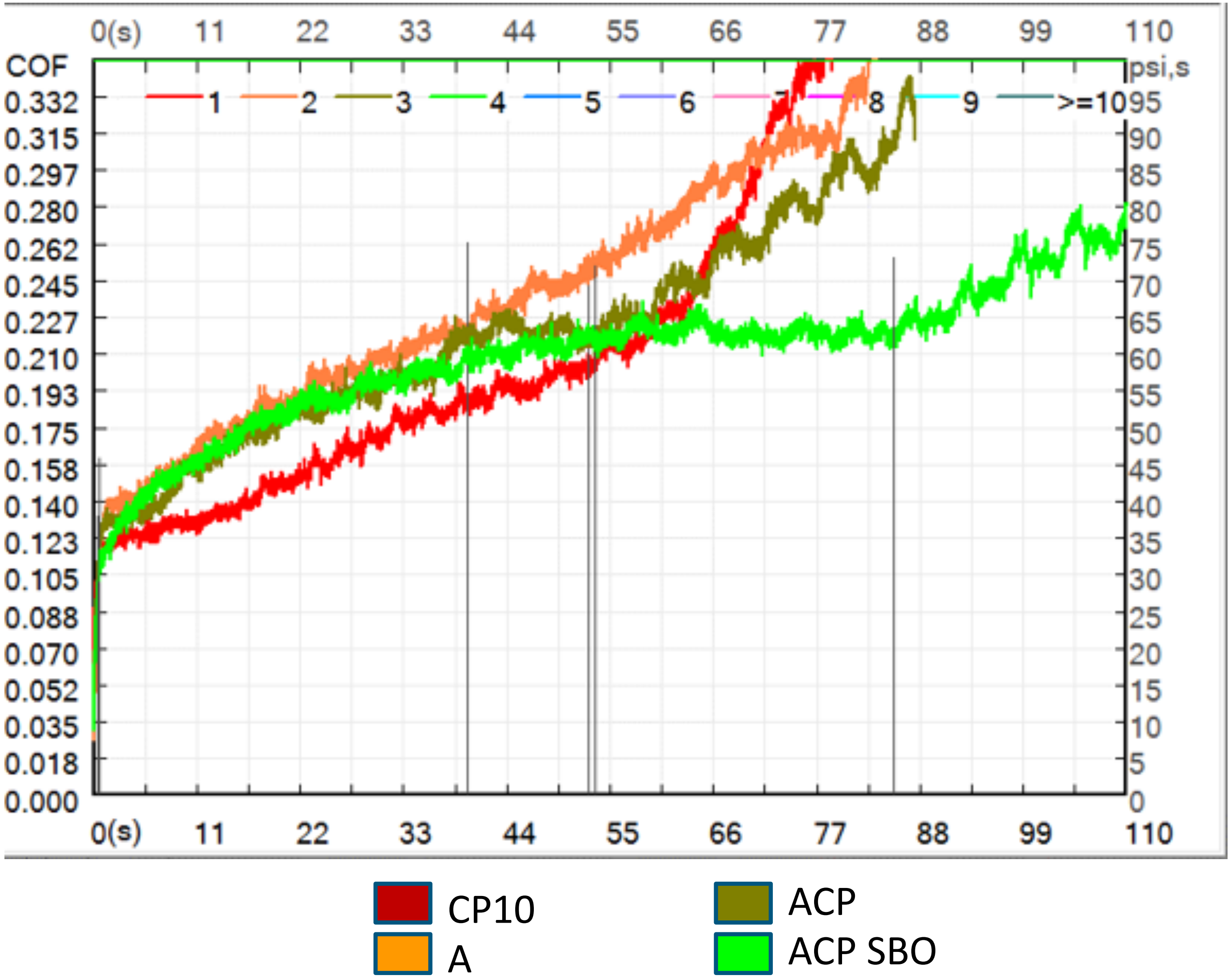


CP10
A
ACP
ACP SBO

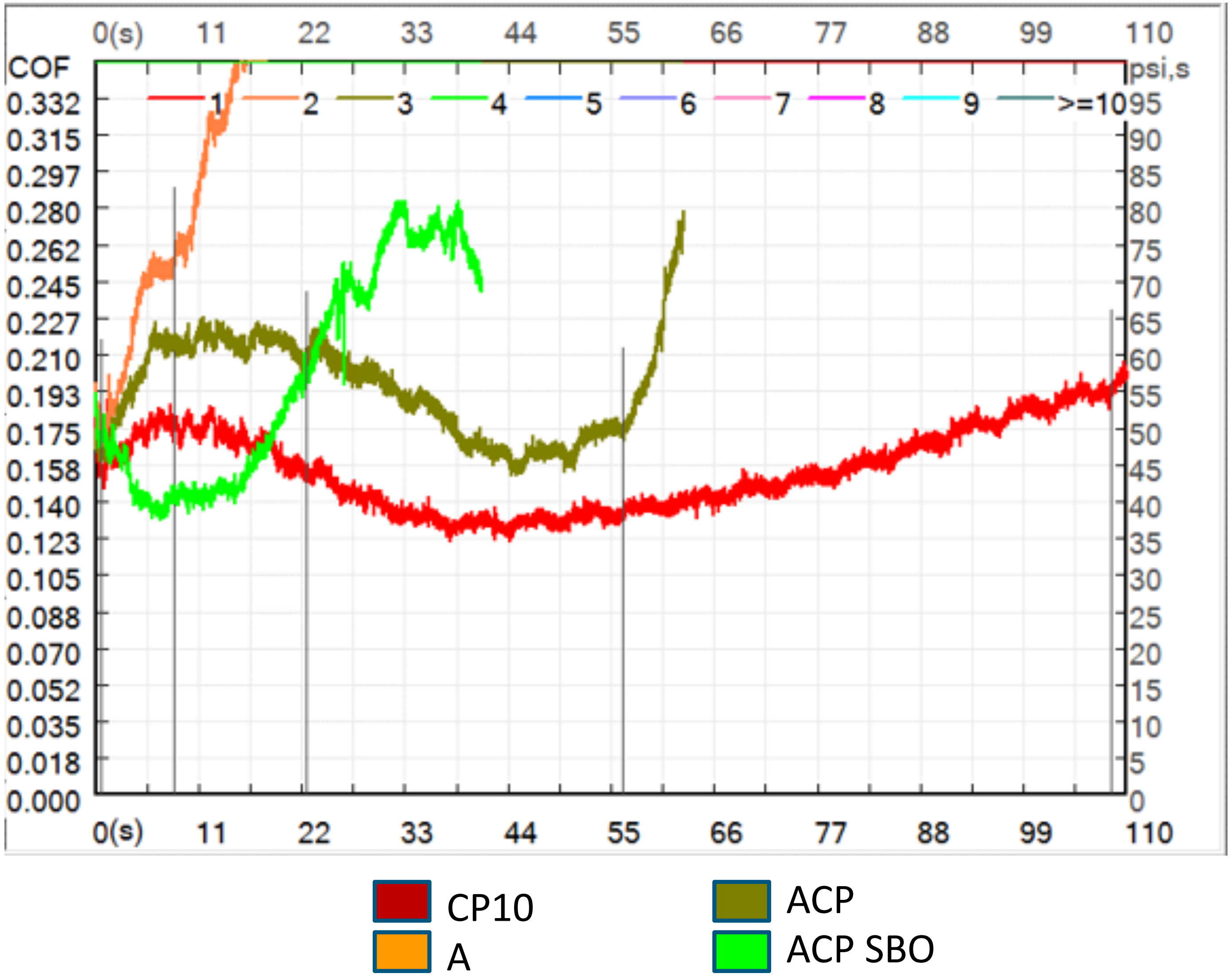
SS 410: 20KSI TCT COF VS TIME GRAPHS



INCONEL 718: 5KSI TCT COF VS TIME GRAPHS



WASPALOY: 5KSI TCT COF VS TIME GRAPHS



TCT FRICTION FACTOR SUMMARY (TBD/(0.8 COFAVG+0.2 COFI))

Metal	Type	CP10	A	ACP	ACP SB0
CRS 1008	Mild Steel	299	263	305	474
DP 600	Dual Phase AHSS	662	466	511	630
SS 409	Ferritic	320	245	509	438
SS 410	Martensitic	93	98	97	162
SS 304	Austenitic	1301	35	73	41
A 286	Fe Based Superalloy	24	15	36	23
Inconel 718	Nickel Based	337	233	305	465
Waspaloy	Nickel Based High Cobalt	645	36	331	133

Worse than CP10 (red) · Approx. Equal to CP10 (black) · Better than CP10 (green)

ADDITIVE SCREENING STRATEGIES

- Design of Experiments (DOE)
  - A planned approach to determine cause and effect relationships and interactions.
  - Applicable to any process with measurable inputs and outputs.

- Mixture DOE: Widely used to balance 3-4 components to optimize formulations

Question: How to select the 3-4 components when test data and experience may be lacking with newer materials?

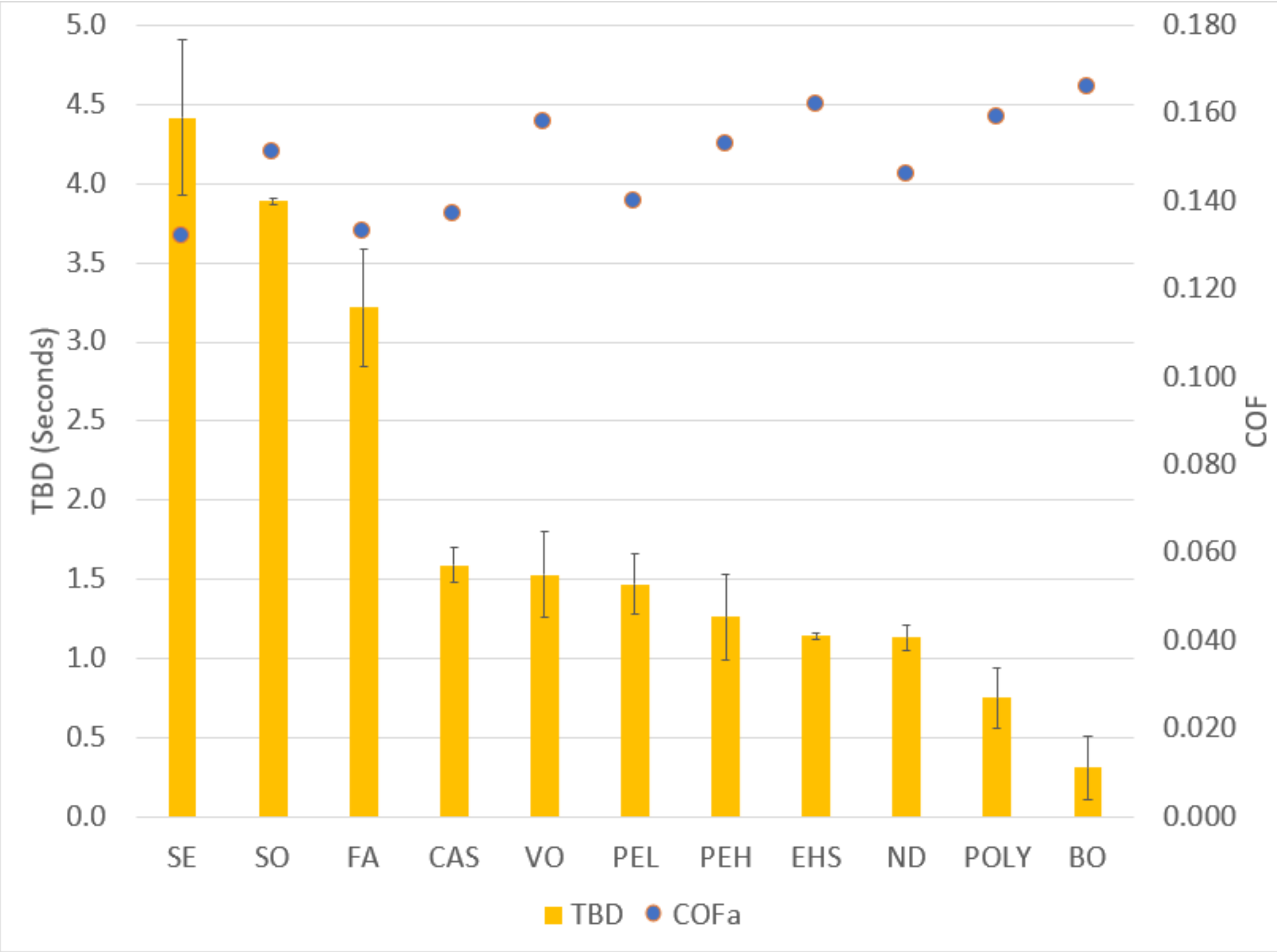
ONE FACTOR AT A TIME (OFAT) SCREENING

- Examples of Applications:
  - Additive responses in various base oils
  - Compare single additive performance at different concentrations
  - Modify existing formulation by addition to improve performance
  - Compare a variety of additives individually

SS 304 OFAT EXAMPLE: TEST INDIVIDUAL ADDITIVES AT A TYPICAL USE CONCENTRATION

Code	Description	%(w/w)
BO	38cSt @ 40°C Naphthenic blend	100.0
SO	37% Sulfurized Olefin, 35% Active	10.0
PEL	C-18 Phosphate Ester AV=150, 4%P, EO	4.0
VO	Vegetable oil: 22% Erucic acid	13.4
EHS	2-ethylhexyl stearate	13.4
SE	Sulfurized triglyceride/olefin 26%S, 15% Active	10.0
PEH	Amine isotridecyl phosphate	4.0
Poly	Polymeric Ester	6.7
FA	Polymerized fatty acid, AV=50	10.0
ND	Nanocarbon dispersion	6.7
CaS	400TBN Calcium Sulfonate	6.7

OFAT INDIVIDUAL INGREDIENT TBD RANKING (SS304/D2 – 2KSI)



OFAT GENERAL OBSERVATIONS

- Advantages:
  - Lowest testing resource for focused investigations
  - Additive incompatibility does not affect the whole test matrix
  - May use with an existing formulation to select additives for further study

- Limitations:
  - Conclusions limited to the single factor at the level tested
  - No information on interactions

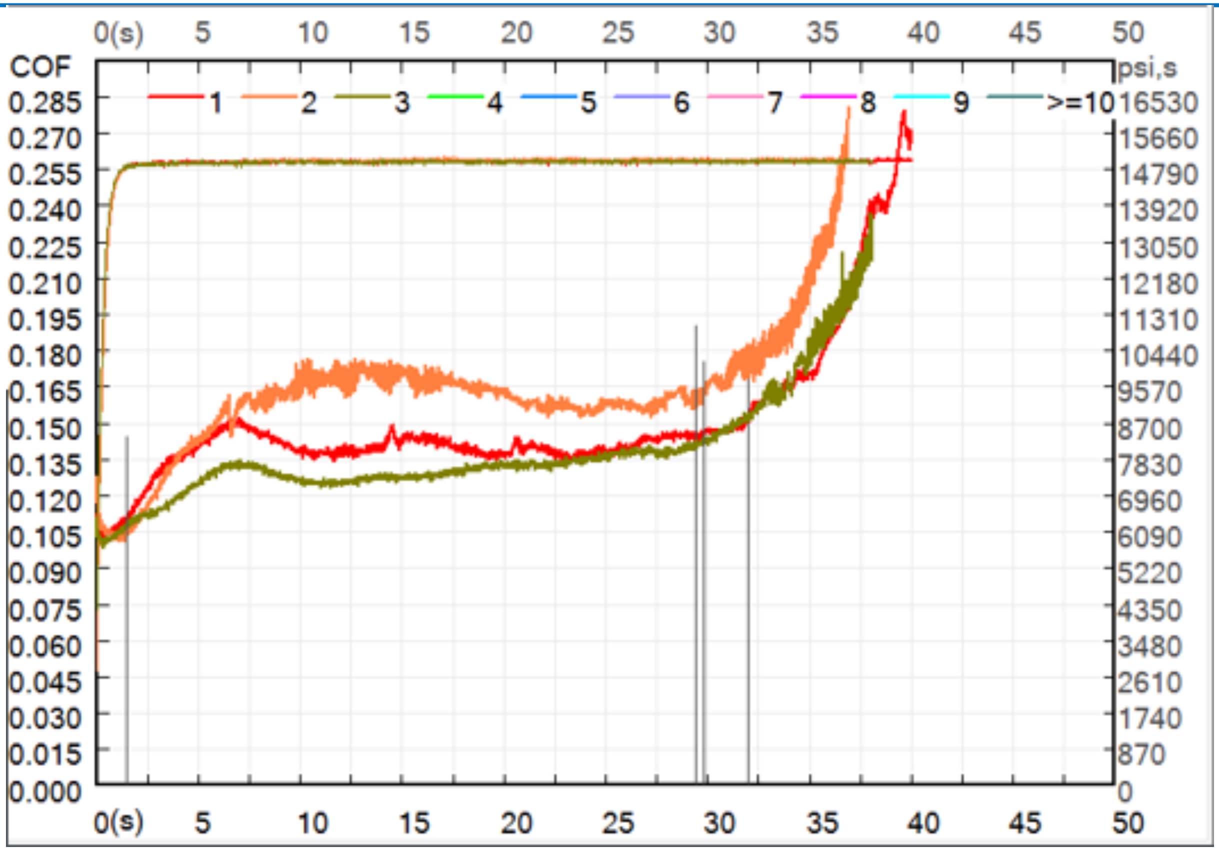
BINARY ADDITIVE SCREENING FOR SYNERGIES AND ANTAGONISMS

- Goal: Identify additives synergistic with 37% active sulfurized olefin on AISI 1008 CRS (15ksi) and SS 304 (3ksi) using TCT
- Process:
  - Test 10% solution of sulfurized olefin
  - Test 5% solutions of additives
  - Test the combination: 10% sulfurized olefin + 5% additive

BINARY SCREENING FOR SYNERGIES EXAMPLE: BLENDS TO 38CST @ 40°C IN NAPHTHENIC BASE OILS

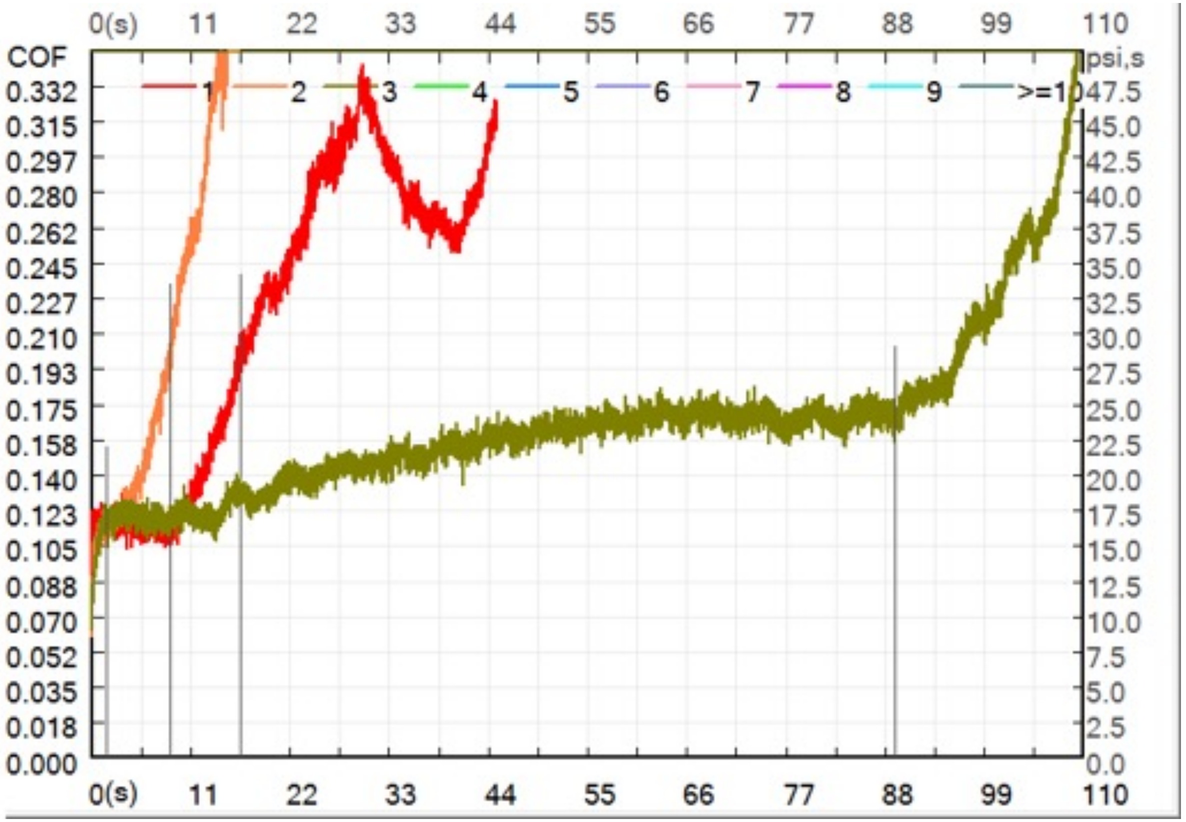
Ingredient	Use Level (%)	Description
S	10	37% Sulfurized Olefin – 35% Active
EA	5	Unsaturated Ester (AV=100)
PE	5	Ethoxylated Phosphate Ester: C-18, AV=150mgKOH/g, 4% Phosphorus
PI	5	Phosphite: AV<5mgKOH/g, 5.4% Phosphorus
Ca	5	Calcium Sulfonate: 400 TBN, 15.5% Calcium

AISI 1008 CRS: SULFURIZED OLEFIN(10%) / CALCIUM SULFONATE(5%): COF VS TIME GRAPHS: 15KSI



Lubricant	COFi	COFa	TBD	COF5	FF
NS	0.111	0.146	29.22	0.145	210
ANCa	0.101	0.154	28.24	0.151	197
NCa	0.104	0.131	26.52	0.132	211

SS 304: SULFURIZED OLEFIN / CALCIUM SULFONATE: COF VS TIME GRAPHS:2KSI



Lubricant	COFi	COFa	TBD	COF5	FF
NS	0.118	0.136	14.42	0.116	109
ANCa	0.114	0.146	6.97	0.163	50
NCa	0.119	0.147	89.48	0.118	633

BINARY SCREENING FOR SYNERGIES AND ANTAGONISMS OBSERVATIONS

- Advantages:
  - Identifies synergies effectively
  - Additive incompatibility does not affect the whole study

- Limitations:
  - Conclusions limited to the additive concentrations tested
  - No information on varying proportions of additive pairs

SCREENING DOE ADDITIVES AND CONSTRAINTS (SAME ADDITIVES AS OFAT EXCEPT CAS SS304 2KSI)

		Constraints	
Code	**Description**	**Lower(%)**	**Upper(%)**
Base	38cSt @ 40°C Naphthenic blend	80	80
A:SO	37% Sulfurized Olefin, 35% Active	0	15
B:PEL	C-18 Phosphate Ester AV=150, 4%P, EO	0	6
C:VO	Vegetable oil: 22% Erucic acid	0	20
D:EHS	2-ethylhexyl stearate	0	20
E:SE	Sulfurized triglyceride/olefin 26%S, 15% Active	0	15
F:PEH	Amine isostricecyl phosphate	0	6
G:Poly	Polymeric Ester	0	10
H:FA	Polymerized fatty acid, AV=50	0	15
J:ND	Nanocarbon dispersion	0	10
	Total A+B+C+D+E+F+G+H+J	**20**	

SCREENING 9 COMPONENT DOE BLENDS: TCT TEST: SS304 2KSI

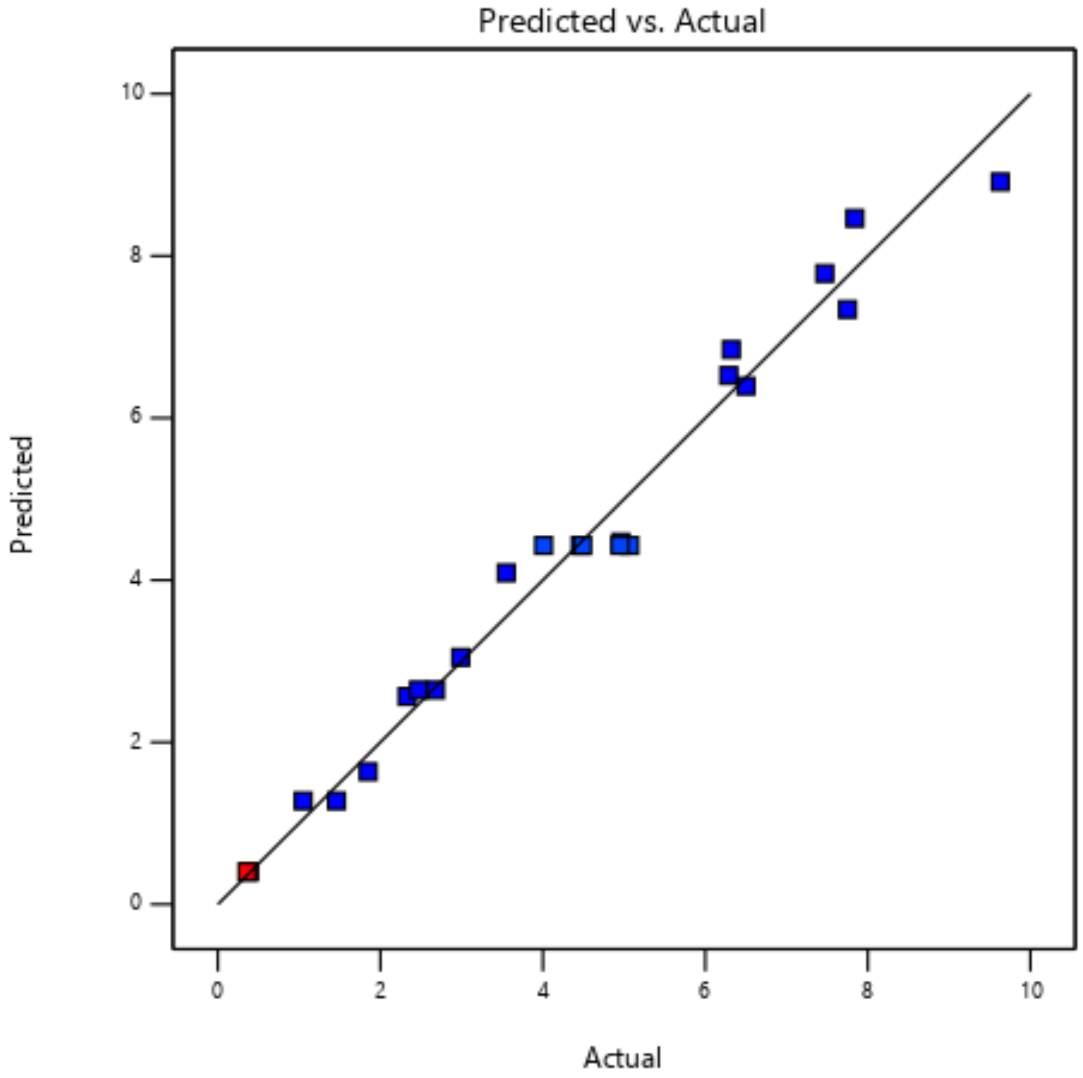
Ingredient	1	2	3	4	5	6	7	8	9	10	11	12	13-14	15	16	17	18	19-23
Base Oil	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
A:SO	0.00	15.00	0.00	0.00	0.00	14.00	0.00	0.00	14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.46
B:PEL	0.00	0.00	6.00	0.00	0.00	6.00	5.00	0.00	0.00	0.00	0.00	0.00	6.00	0.00	6.00	0.00	0.00	2.18
C:VO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.00	0.00	0.00	0.00	4.00	0.00	20.00	1.30
D:EHS	0.00	0.00	0.00	0.00	20.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.00	0.00	1.30
E:SE	0.00	0.00	14.00	4.00	0.00	0.00	0.00	0.00	0.00	15.00	0.00	14.00	0.00	0.00	0.00	0.00	0.00	2.46
F:PEH	6.00	0.00	0.00	6.00	0.00	0.00	0.00	0.00	6.00	0.00	0.00	6.00	6.00	0.00	0.00	0.00	0.00	2.18
G:Poly	0.00	5.00	0.00	10.00	0.00	0.00	0.00	10.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	0.00	2.82
H:FA	14.00	0.00	0.00	0.00	0.00	0.00	15.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	0.00	0.00	2.46
J:ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	5.00	0.00	0.00	8.00	10.00	0.00	0.00	0.00	2.82
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

- Design includes some combinations of additives (2-3)
- Two additives are tested individually (VO, EHS)
- Includes a reference blend (19-23) includes all factors (additives)
  - Replicates are included to estimate pure error

SCREENING MIXTURE DOE ANOVA AND LINEAR MODEL

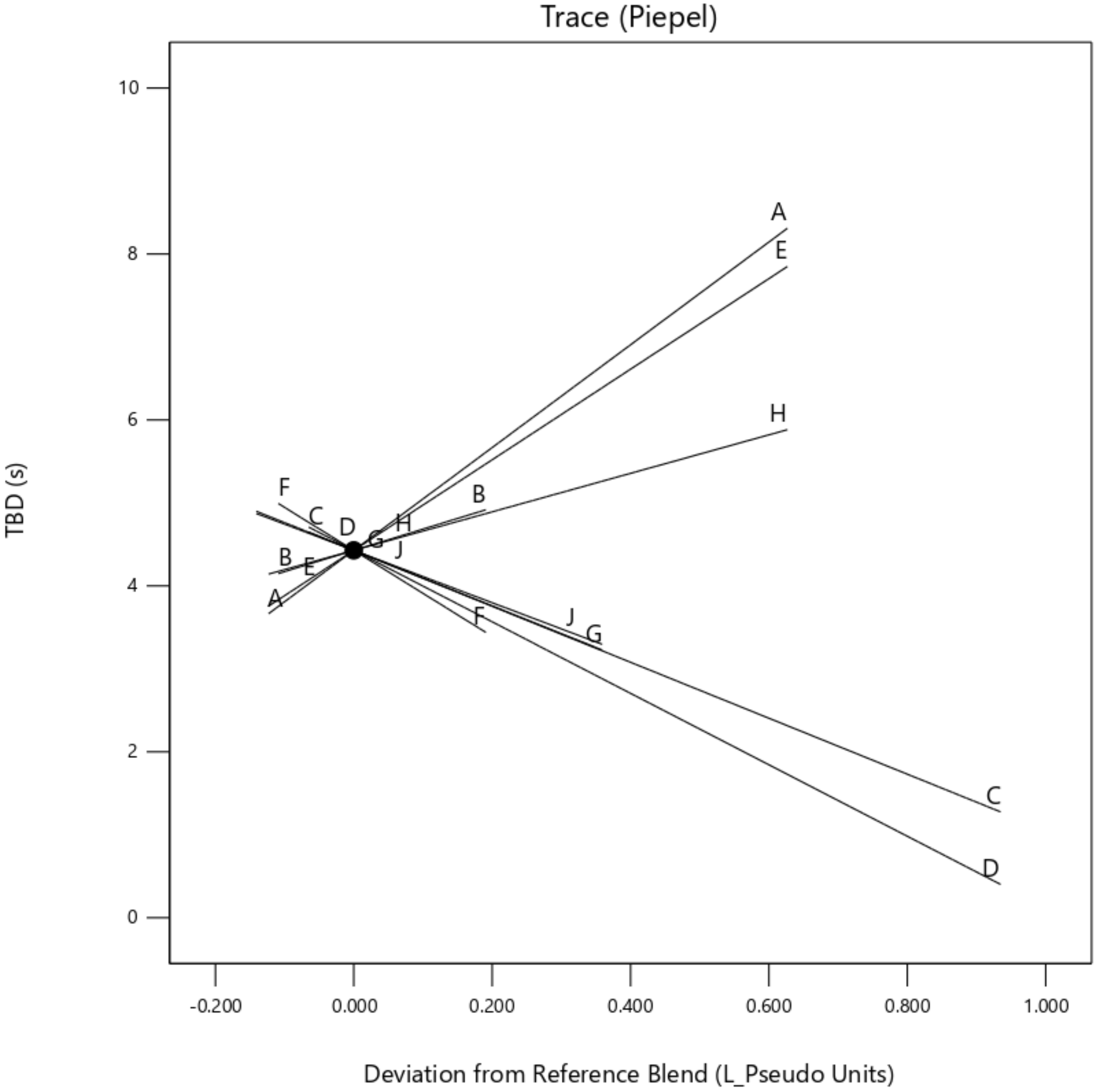
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	141.82	8	17.73	79.31	< 0.0001	significant
[1] Linear Mixture	141.82	8	17.73	79.31	< 0.0001	
Residual	3.13	14	0.2235			
Lack of Fit	2.30	7	0.3285	2.77	0.1010	not significant
Pure Error	0.8297	7	0.1185			
Cor Total	144.94	22				

TBD	=
+0.492973	* SO
+0.335669	* PEL
+0.063830	* VO
+0.020115	* EHS
+0.460737	* SE
-0.009307	* PEH
+0.077783	* Poly
+0.323162	* FA
+0.085914	* ND



SCREENING MIXTURE DOE TCT TBD TRACE PLOT: SS304 2KSI

Component	Reference Blend %
Base Oil	80.00
A:SO	2.46
B:PEL	2.18
C:VO	1.30
D:EHS	1.30
E:SE	2.46
F:PEH	2.18
G:Poly	2.82
H:FA	2.46
J:ND	2.82
Total	100.00



Component	Gradient (Real)
A:SO	6.19
E:SE	5.46
B:PEL	2.56
H:FA	2.32
J:ND	-3.15
G:Poly	-3.34
C:VO	-3.37
D:EHS	-4.31
F:PEH	-5.18

THREE COMPONENT MIXTURE DOE EXAMPLE

Goal: Maximize TCT time until lubricant film breakdown (TBD) with AISI 1008 CRS @ 25ksi

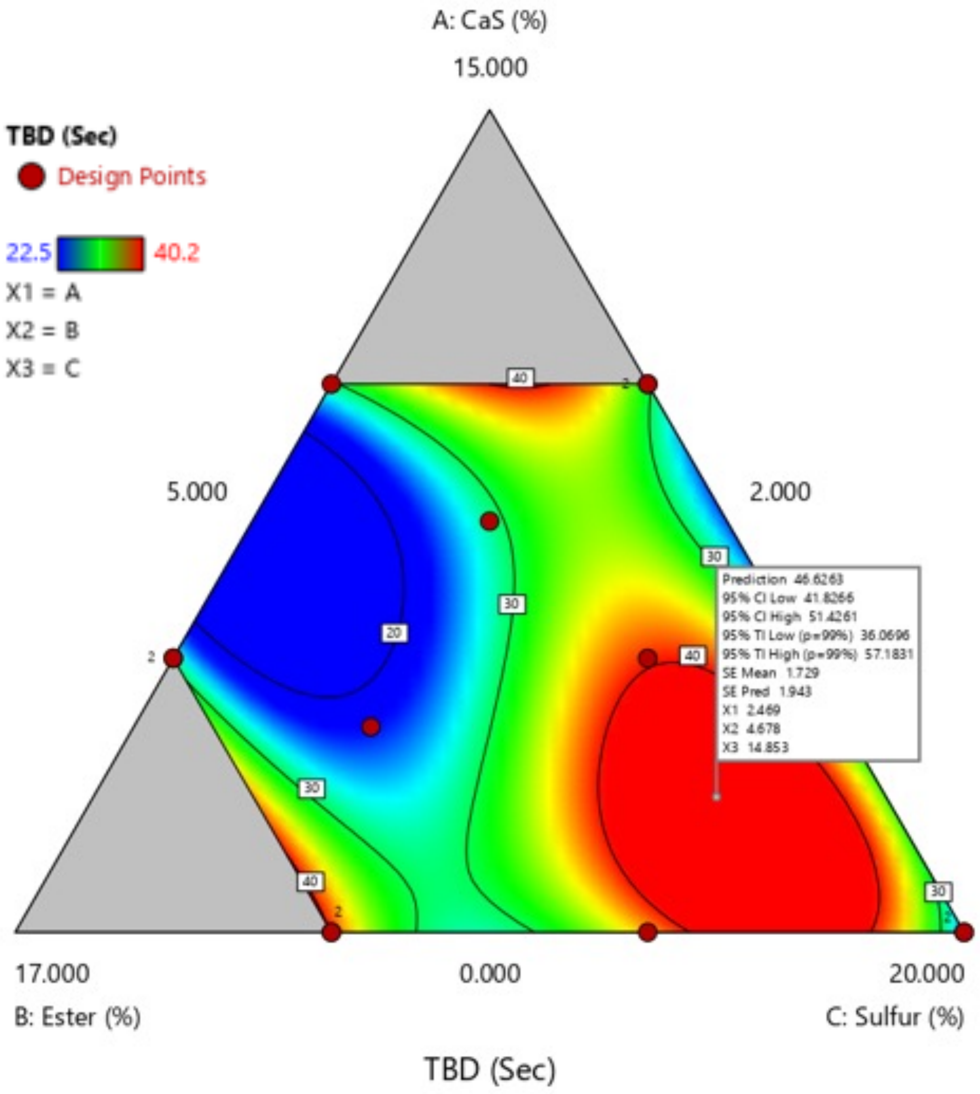
Run #	Ca	Ester	S pkg
1	0	2	20
2	5	12	5
3	10	2	10
4	0	12	10
5	10	7	5
6	5	4.5	12.5
7	0	7	15
8	3.75	9.5	8.75
9	7.5	5.75	8.75
10	5	2	15
11	0	12	10
12	5	12	5
13	0	2	20
14	10	2	10

Design Space

Component	Low Limit		Constraint		High Limit
300 TBN Calcium Sulfonate	0.00	≤	A: CaS	≤	10.00
C-18 Glycerol Ester	2.00	≤	B: Ester	≤	12.00
Sulfurized Olefins (21.8% Total S/ 4.8% Active)	5.00	≤	C: Sulfur	≤	20.00
			A+B+C	=	22.00

TIME UNTIL BREAKDOWN (TBD) CONTOUR GRAPH: 1008 CRS

- Optimum Blend region to maximize TCT TBD
- A:CaS = 2.5%
- B:Ester = 4.6%
- C:Sulfur = 14.9%



THREE COMPONENT DOE OBSERVATIONS

- Advantages:
  - Efficient use of testing resources : Models all of design space
  - Identifies “sweet spots” and regions to avoid in design space
  - Identifies and models additive interactions
  - Can be used to optimize multiple responses (TBD, COFavg, and cost for example)
- Limitations (Planning considerations):
  - Not a practical screening tool (min. 55 tests required for 9 additives)
  - Additives must be compatible across all of design space

SCREENING STRATEGY SUMMARY: 9 ADDITIVES

Screening Strategy	Tests Required for 9 Additive Screen	Conclusion(s)
OFAT Individual Adds or Add to Product	10 (9 + Base)	Efficient for specifically defined data requirement(s)
2-factor Synergy with Single Additive (SO)	19 (9 Individual + 9 Combinations + SO)	Gives specific compatiblilty ranking with a single additive
DOE Screening	23	Efficient: Information about levels and general compatibility of additives. Linear models only. Non-statistical observations also useful
9 Component full DOE	55	Deeper understanding of levels and interactions: For reference
3 Component full DOE	14-20	For reference

SUMMARY

- Complete, cost-effective, CP replacement will be extremely challenging for certain critical applications and materials
- Careful selection and validation of tribotests are necessary
- Several screening techniques are available
  - Basestocks
  - Additives
- Mixture DOE is useful for optimizing selected additive levels

ACKNOWLEDGEMENTS

THANK YOU!

ILMA MWF Conference Organizers and Sponsors

Sea-Land Chemical Co. / SLC Testing Services

Questions?

Ted McClure
Sea-Land Chemical Co / SLC Testing Services
18013 Cleveland Parkway
Cleveland, OH 44135
(440) 871-7887
ted.mcclure@sealandchem.com