The Role Additive Chemistry Plays in Increasing and Decreasing Timing Chain Wear

C. Esche, S. Donnelly, V. Gatto, G. Mazzamaro,
M. Patel, S. Tung

Vanderbilt Chemicals, LLC
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Problem

- T-GDI engines are experiencing higher than normal timing chain wear
  - The timing chain with the vanadium carbide coating tends to experience the higher wear
  - Timing chain pin coated
    - Link not coated

Background

- Industry speculation
  - Corrosion related
    - Incomplete combustion leads to acidic by-products that promote wear
  - Soot caused by incomplete combustion causes significant and measurable wear
- Not all timing chain coatings respond the same way
  - Some are more affected by soot
  - Others more affected by acidic compounds

Objectives

- Identify root cause(s) and/or solution(s) to the timing chain wear problem using a bench test
  - Develop wear hypothesis
- Work jointly with OEM chain supplier
  - Developed and run the bench test
  - Provided following information
    - Engine oils with typical phosphorus level have unacceptable wear
    - Low phosphorus engine oils tend to have low wear but don't know why

Bench Test Conditions

- Temperature: 93C
- Soot, carbon black: 0.15 wt.%
- Lube Oil Rate: 1 liter per minute
- Test Load: 1000 N
- Test Speed: 6500 RPM
- Test Duration:100 hours

- Center Distance measurement used to determine % Elongation
- In the beginning first 5 test oils were run twice but because of good test repeatability only once thereafter
- No acid used in this bench test
- Pin coating is OEM chain company specific
- OEM chain supplier ran the bench test

Wear Mechanism Hypothesis

- Unknown chemical wear initiation reaction
  - Zinc encourages
  - Molybdenum suppresses
    - Boron less effective than molybdenum
- Soot and or acid function as wear accelerators
- Phosphorus antiwear additives not needed to prevent timing chain wear
    - Engine oil containing only 65 ppm phosphorus, from MoDDP, performed very well
      - No ZDDP in formulation
    - Antiwear film formation not necessary to protect timing chain

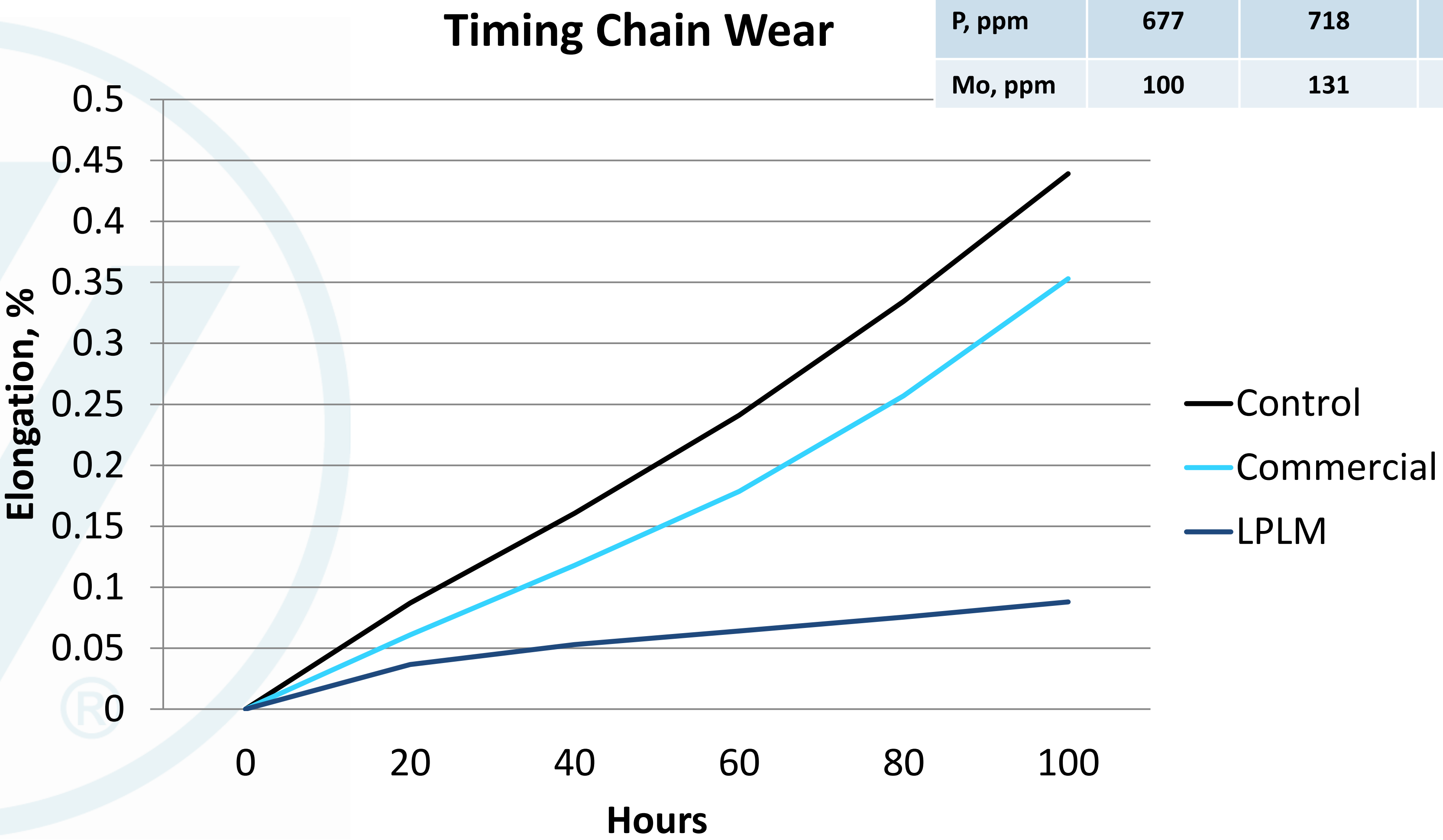
Engine Oil Wear Baselines

- Confirm OEM chain supplier low phosphorus oil observation
  - Self formulated a low phosphorus low molybdenum (LPLM 1) oil
- Compare the LPLM 1 oil results to a commercial oil purchased off the shelf and a self formulated control oil
  - Both the commercial and Control Oil 1 are high phosphorus, low molybdenum oils
- LPLM oil delivered significantly improved wear over the Control and Commercial oils.
  - Validated low phosphorus oil observation
  - Investigate ZDDP
- Control Oil 1 delivered similar results to the Commercial Oil and therefore can be modified as needed for wear testing

	Control Oil 1	Commercial Oil 1	LPLM 1
P, ppm	677	718	229
Mo, ppm	100	131	102

Engine Oil Baseline Performance

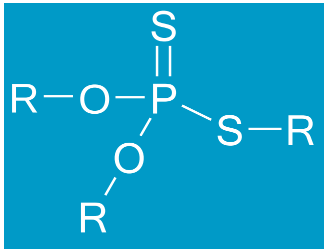
	Control Oil 1	Commercial Oil	LPLM 1
P, ppm	677	718	229
Mo, ppm	100	131	102



ZDDP Dissection

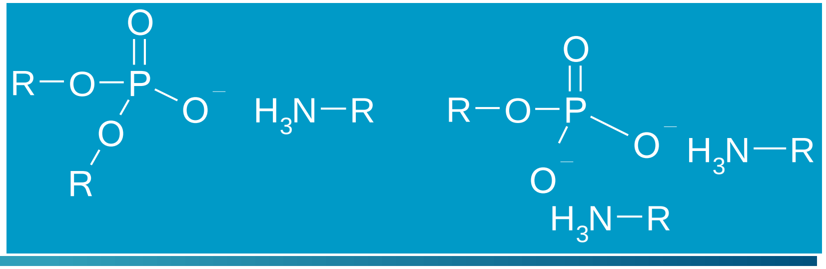
- Zinc Dialkyl Dithio-Phosphate (ZDDP) is a commonly used antiwear engine oil additive
- Contains zinc, sulfur and phosphorus
- Identify what part of the ZDDP molecule is the bad actor
- Modified Control Oil 1
  - Alkylthio Phosphate Thioester (APT)
  - Amine Salt of Alkylphosphate (ASA)
- Test data showed zinc plays major role in promoting wear
  - Phosphorus and sulfur minimal influence
- Known in the industry that ZDDP forms film significantly faster than other phosphorus antiwear additive
  - Supports film formation not significant factor in preventing wear hypothesis
  - Formation of a super abrasive calcium phosphate coated soot particle not critical path to high wear
    - Supported by calcium sulfonate experiment

	Expt'l Oil 1	Expt'l Oil 2	Control Oil 1
	APT	ASA	ZDDP
P, ppm	729	687	677
Sulfur	1500	300	1400
Zinc	<1	<1	757
Mo, ppm	98	98	100



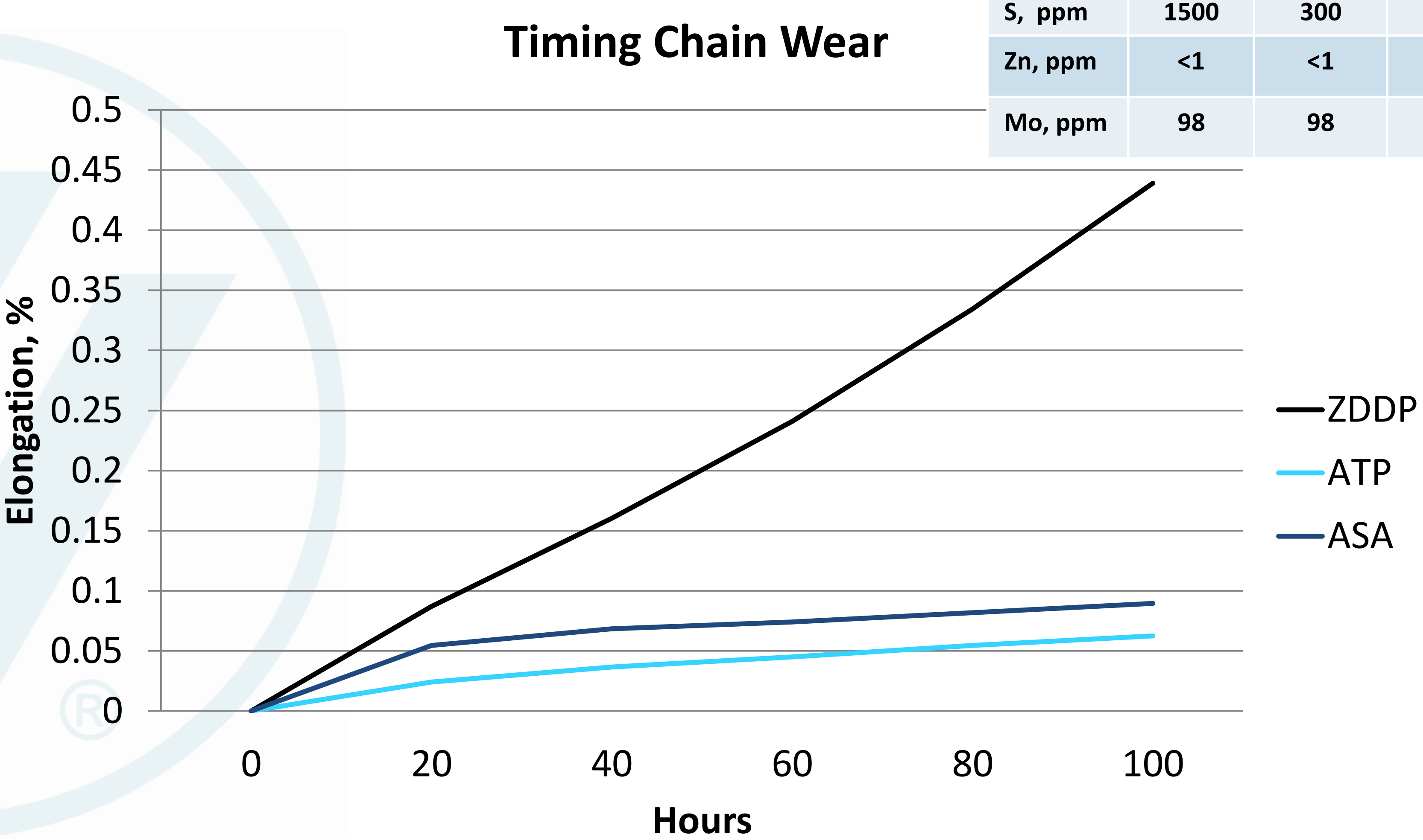
← APT

ASA ↓



ZDDP Dissection

	ATP	ASA	ZDDP
P, ppm	729	687	677
S, ppm	1500	300	1400
Zn, ppm	<1	<1	757
Mo, ppm	98	98	100



Zinc Treat Rate Effect

- A 50% reduced zinc finished oil was prepared using both APT and ZDDP but at half their respective treat rate
  - Phosphorus, sulfur and molybdenum levels are constant
- Test data showed timing chain wear highly sensitive to zinc level

	Expt'l Oil 1	Expt'l Oil 3	Control Oil 1
	APT	APT/ZDDP	ZDDP
P, ppm	729	690	677
S, ppm	1500	1400	1400
Zn, ppm	<1	340	757
Mo, ppm	98	102	100

Zinc Treat Rate Effect

	Expt'l Oil 1	Expt'l Oil 3	Control Oil 1
	APT	APT/ZDDP	ZDDP
P, ppm	729	690	677
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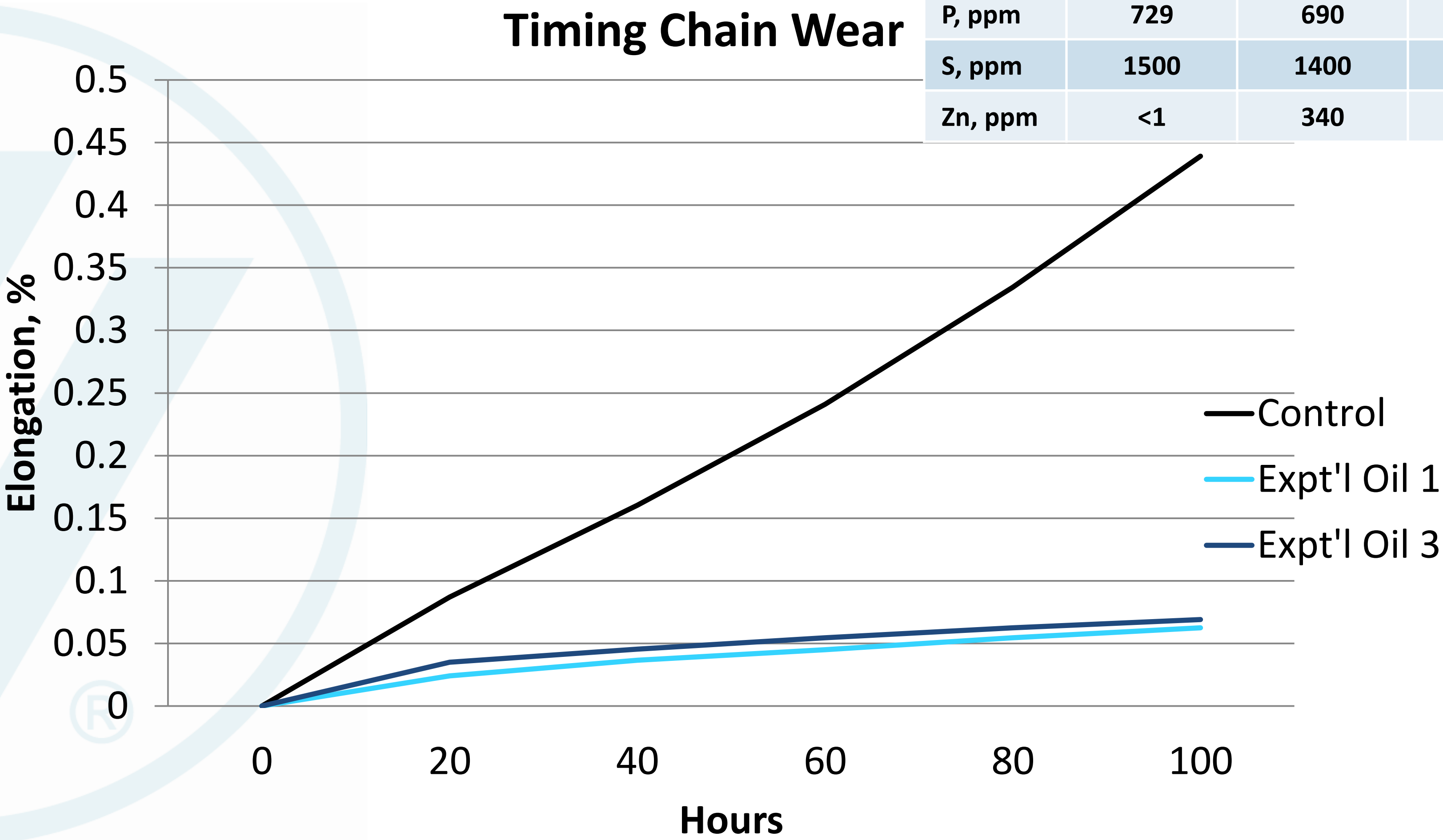
Zn, ppm	<1	340	757



Molybdenum Effect

- Look at effect molybdenum has on timing chain wear
  - Known supplemental antiwear additive
- Modified Control Oil 1 with same molybdenum friction modifier but at a higher level
- Test data showed molybdenum played significant role in reducing wear

	Expt’l Oil 4	Control Oil 1
MoFM Type	Mo E/A	Mo E/A
P, ppm	682	677
Mo, ppm	684	100

Molybdenum Effect

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MoFM Type	Mo E/A	Mo E/A
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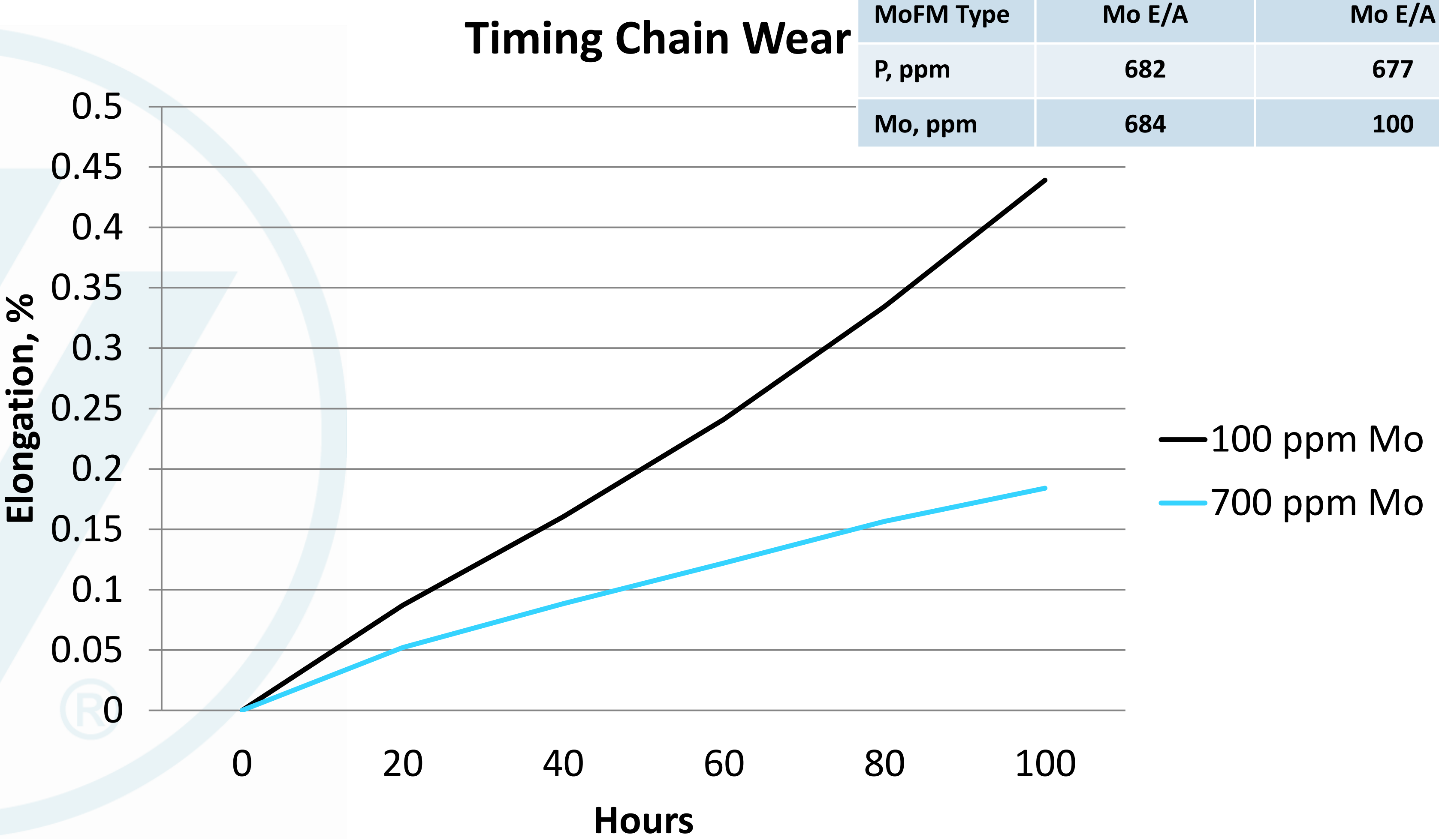


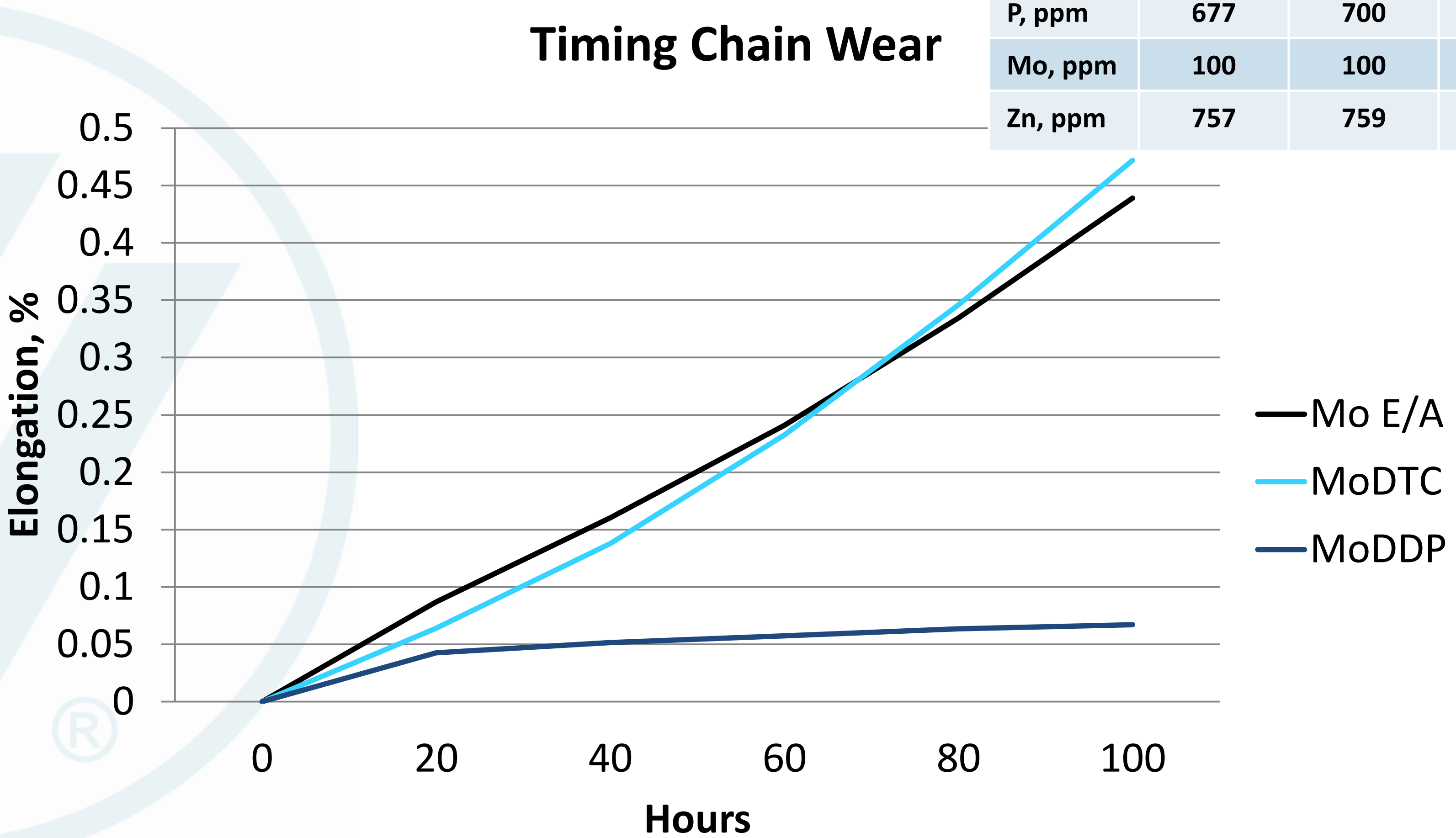
Other Molybdenum Additives

- Evaluate performance of other molybdenum friction modifiers in Control Oil
  - MoDTC and MoDDP
- MoDDP containing oil delivered excellent wear in a low phosphorus oil
  - Phosphorus antiwear film not needed for wear protection
  - Suggest non-antiwear film mechanism protects timing chain from wear
  - Soot related wear should have been magnified without antiwear film
  - Suggests chemical reaction mechanism key to wear

	Control Oil 1	Expt'l Oil 5	Expt'l Oil 6
MoFM	Mo E/A	MoDTC	MoDDP
P, ppm	677	684	65
Mo, ppm	100	100	96
Zn, ppm	757	759	<1

Other Molybdenum Additives

	Control Oil 1	Expt'l Oil 5	Expt'l Oil 6
MoFM	Mo E/A	MoDTC	MoDDP
P, ppm	677	700	65
Mo, ppm	100	100	100
Zn, ppm	757	759	<1



2 Factor by 2 Level Matrix Design

- Test design:
  - Same oil formulation style
  - Molybdenum levels: 100 and 700 ppm
  - Zinc Levels: 250 and 750 ppm
- Test results for one time pass
  - Coded Coefficients Effect:
    - Zn: +0.18600
    - Mo: -0.09000
    - Zn:Moly Interaction: -0.16500
  - Suggests chemical reaction mechanism

Boron Effect

- Boron known in the industry to have antiwear activity
  - Expt'l Oil 7 contains 105 ppm boron from a borated organic friction modifier (OFM)
  - Expt'l Oil 8 contains boron from borated dispersants and a borated OFM
    - Low phosphorus oil confirms antiwear film not needed to prevent wear even in high zinc enviroment
- Boron containing oils showed significant wear reduction versus the control oil
  - Suggests chemical versus antiwear film mechanism

	Control Oil 1	Expt'l Oil 7	Expt'l Oil 8
P, ppm	677	687	244
Mo, ppm	100	<1	685
Zn, ppm	757	763	834*
B, ppm	4	105	271

* = zinc from ZDDP and ZnDTC and oil was supplied to us and is a different formulation style than the Control Oil

Boron Effect

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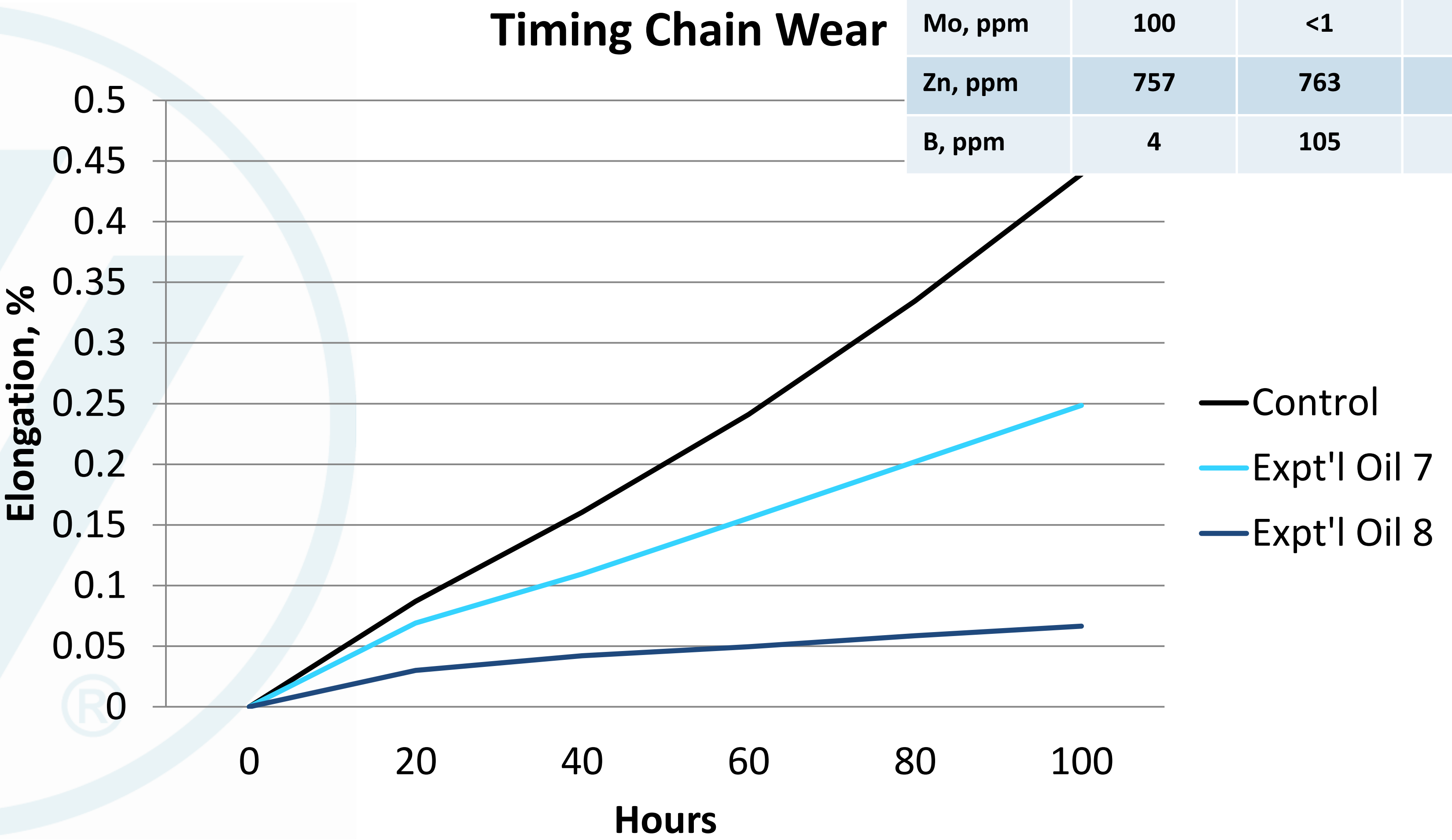

No Detergent Effect

- Overbased calcium sulfonate removed from the Control Oil to test theory that a hard calcium phosphate coating on the soot was responsible for the wear
  - Low TBN oil
- Initially, wear was similar for both oils but over time wear appears to increase exponentially
  - Need longer test to confirm observation
- Calcium sulfonate not acting as a TBN source since no acid used in bench test
- Calcium sulfonate role unknown at this time

	Expt'l Oil 9	Control Oil 1
P, ppm	700	677
Mo, ppm	100	100
Ca, ppm	3	2400

No Detergent Effect

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P, ppm	700	677
Mo, ppm	100	100
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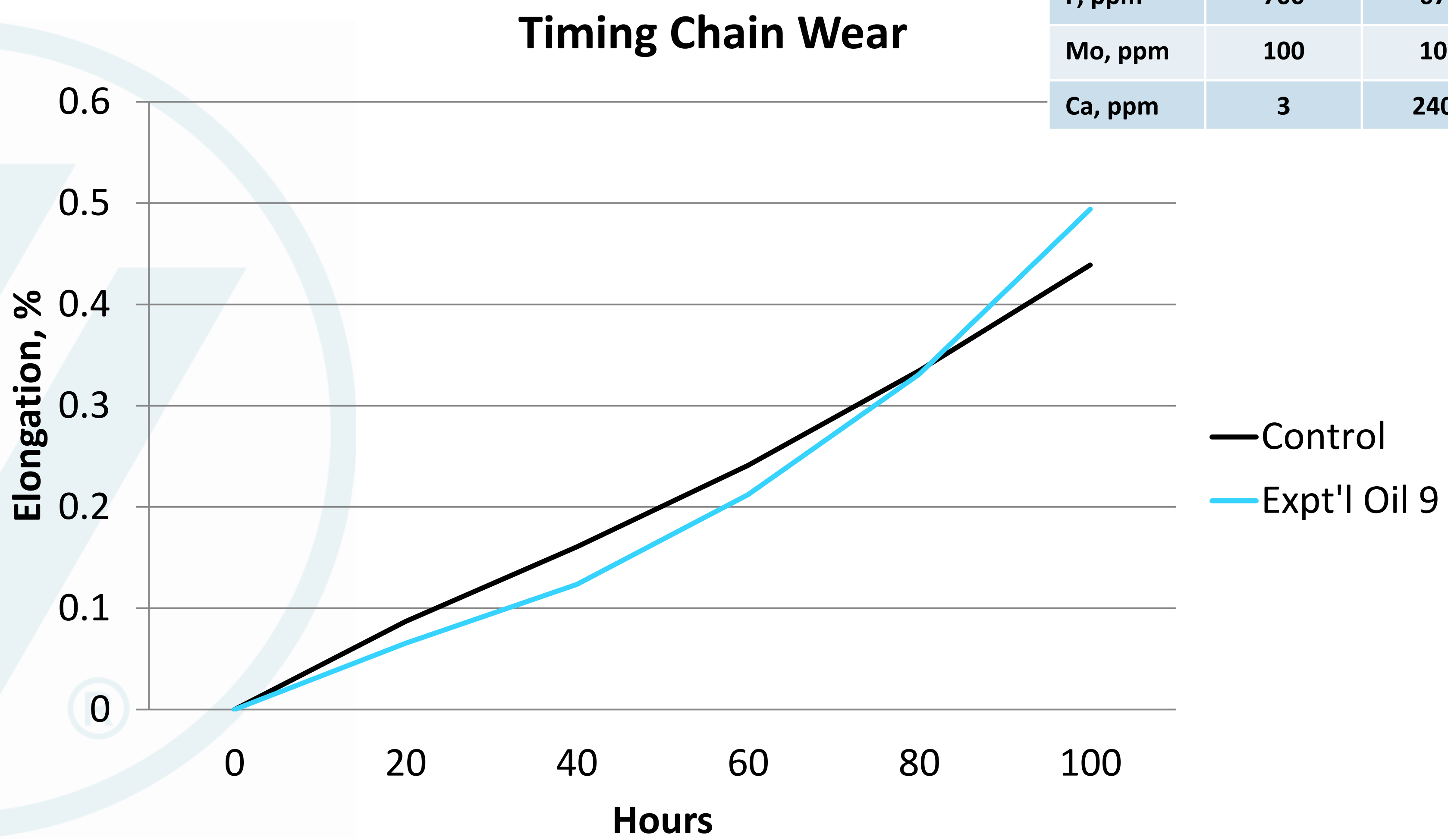


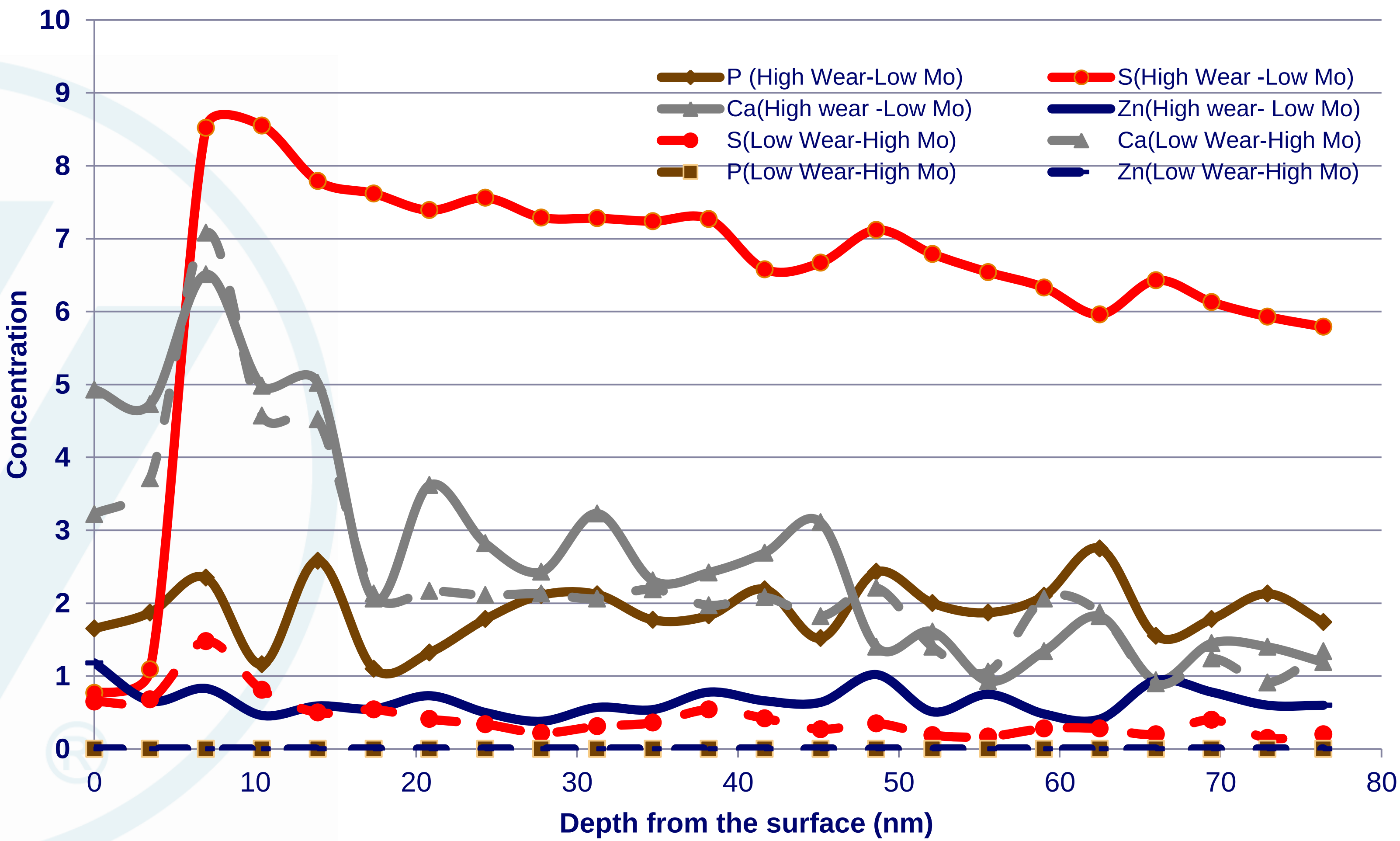
Auger Analysis

- Auger analysis to look at metals on wear surface
  - Control Oil and Expt'l Oil 8
  - Book end test oils for wear performance
- No molybdenum found on wear metal surface for both oils
  - Molybdenum additives known to form a film
  - Suggests non-antiwear film mechanism to prevent wear

	Control Oil 1	Expt'l Oil 8
P, ppm	677	244
Mo, ppm	100	685
Zn, ppm	757	834*
B, ppm	4	271
S, ppm	1400	1400

* = zinc from ZDDP and ZnDTC and oil was supplied to us and is a different formulation style than the Control Oil

Augur Test Results For Expt'l Oils 1 and 8



Summary & Wear Mechanism Hypothesis

- Unknown chemical wear initiation reaction
  - Zinc encourages
    - Small amount of zinc
  - Molybdenum suppresses
    - Boron less effective
  - Soot and or acid function as wear accelerators in the chemically modified environment
    - Zinc carboxylate and zinc absorbed onto soot particle
  - Phosphorus antiwear additives not needed to prevent timing chain wear
    - Engine oil containing only 65 ppm from MoDDP performed very well
  - Antiwear film formation not necessary to protect timing chain