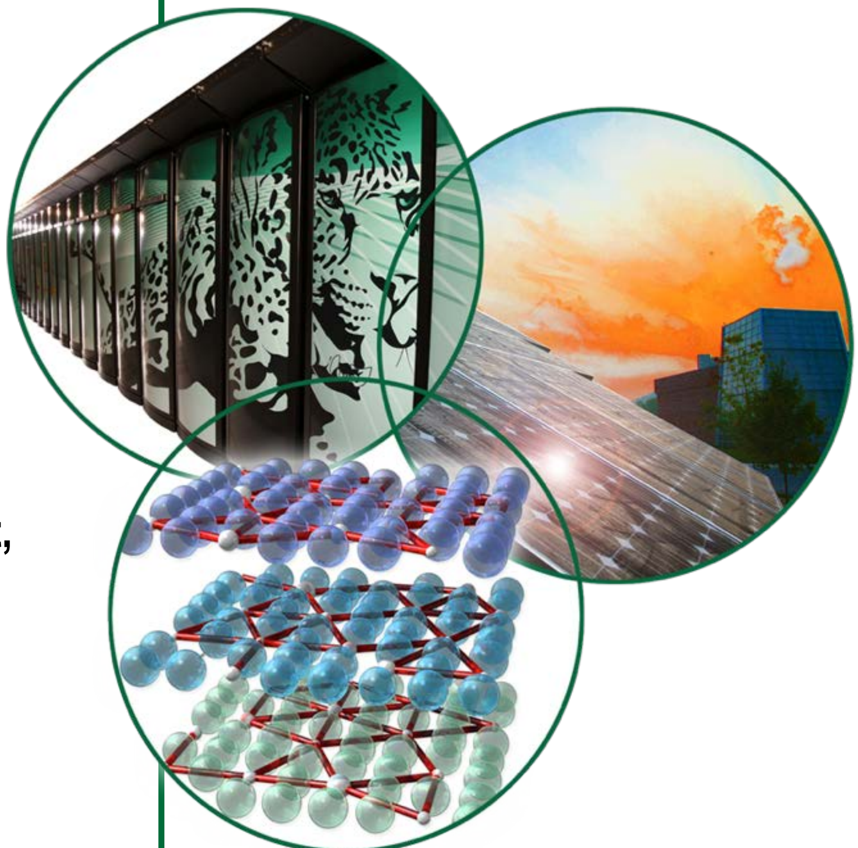
Ionic Liquids as Engine Lubricant Additives, Impact on Emission Control Catalysts, and Compatibility with Coatings



Project ID: FT014

ORNL: Jun Qu, Todd Toops, Huimin Luo, Brian West, Harry Meyer, Donovan Leonard, William Barnhill, Yan Zhou, and William Brookshear

Shell: Bassem Kheireddin and Hong Gao

DOE HQ Program Manager: Kevin Stork

2016 DOE Vehicle Technologies Program Annual Merit Review, June 8, 2016

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- FOA with Shell: Ionic liquids as multi-functional lubricant additives to enhance engine efficiency
  - Duration: July 23, 2012 – December 31, 2015
  - Percent complete: 100%
- AOP: ongoing but re-focused each year to address current DOE and industry needs
  - Task 1: Lubricant effects on emissions control technologies
  - Task 2: Compatibility of lubricant anti-wear additives with hard coatings

Budget

- FOA with Shell
  - Total project funding: DOE share: $1.2M + Shell in-kind cost share: $400K
  - FY15 funding: DOE share: $270K (carryover from FY14) + Shell in-kind cost share: $130K
  - FY16 funding: $0 (project completed)
- AOP
  - FY15 funding: $450K
  - FY16 funding: $400K

Barriers

- Low-viscosity engine oils improve engine fuel economy but increase boundary friction and wear.
- Inadequate data on long-term impact of lubricants on engines and emissions control systems.
- Lack of understanding of the compatibility of lubricant anti-wear additives with non-metallic coatings.

Partners

- FOA/CRADA partner: Shell Global Solutions (US)
- Other collaborators: Cytec, Chevron, Lubrizol, NCT, IonBond, Eaton, Hardcoat, ANL, UT, and PSU

Relevance

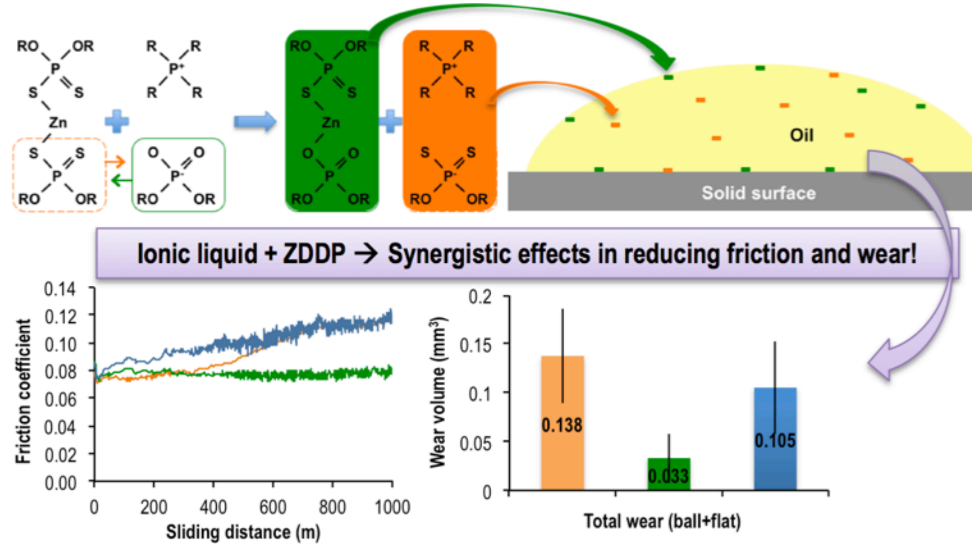
- **To develop oil-soluble ionic liquids (ILs) as engine oil additives to improve the mechanical efficiency of IC engines.**
- **To enable broad acceptability of new lubricant formulations it is important to demonstrate compatibility with modern emissions control systems**
- **To investigate the compatibility of lubricant anti-wear (AW) additives, specifically conventional ZDDP and newly developed ionic liquids, with selected hard coatings.**
- **Fundamental understandings gained in this study will help guide future development of engine lubricants.**

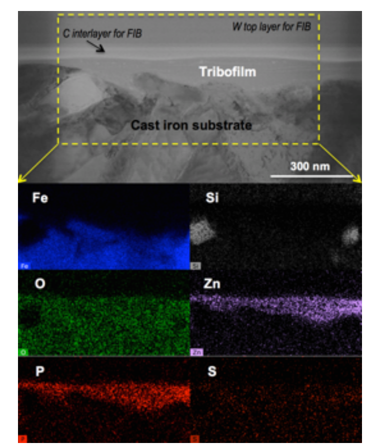
Milestones

- **Design formulated engine lubricants that are compatible with ionic liquid additives (12/31/2014)** ***Completed***
- **Install and commission new stoichiometric gasoline genset for lubricant compatibility investigations (3/31/2015)** ***Completed***
- **Conduct tribological testing and analysis of the AW-coating pairs of interest in mixed friction regime (3/31/2015)** ***Completed***
- **Demonstrate improved fuel economy without sacrificing wear protection for a fully-formulated lubricant containing IL additives using multi-cylinder engine dynamometer tests (6/30/2015)** ***Completed***
- **Correlate experimental and modeling results to reveal the mechanisms behind the AW-coating compatibility (9/30/2015)** ***Completed***
- **Investigate TWC compatibility of new IL formulation both independently and when mixed with ZDDP and compare it to ZDDP-only lubricant additives (12/31/2015)** ***Completed***

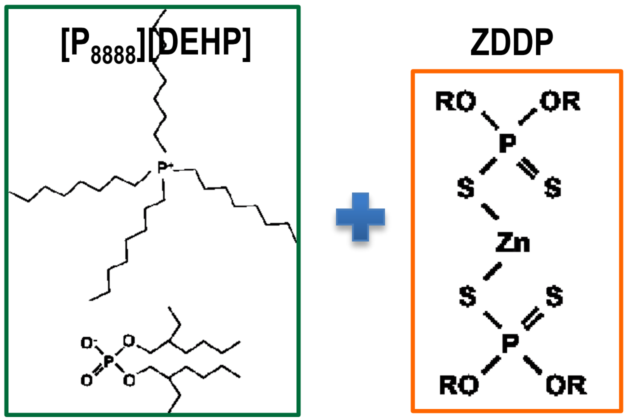
Approach – Ionic liquids as multi-functional lubricant additives to enhance engine efficiency (FOA/CRADA w/ Shell)

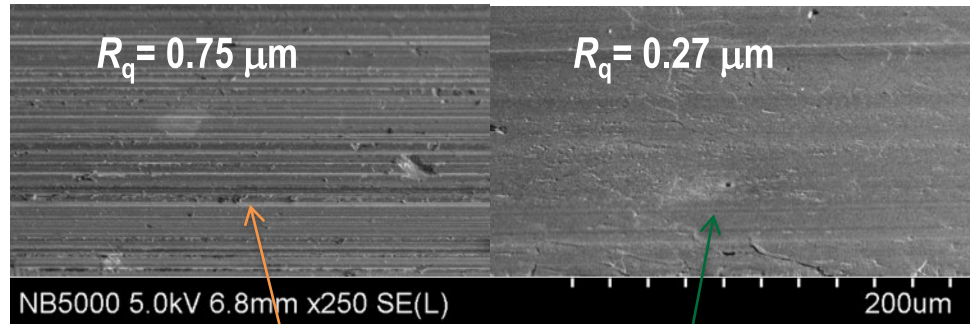
- Several groups of oil-miscible ionic liquids (ILs) had been developed and demonstrated effective anti-wear functionality in tribological bench tests in FY 2012-2014.
- FY 2015-2016 efforts focused on
  - Combining various ILs and ZDDP to seek synergetic effects;
  - Investigating the mechanisms behind the IL+ZDDP synergism;
  - Exploring compatibilities of IL and IL +ZDDP with other additives in the engine oil formulation;
  - Formulating a prototype low-viscosity (SAE 0W-16) engine oil using IL+ZDDP;
  - Demonstrating fuel economy improvement in both tribological bench and engine dynamometer tests.

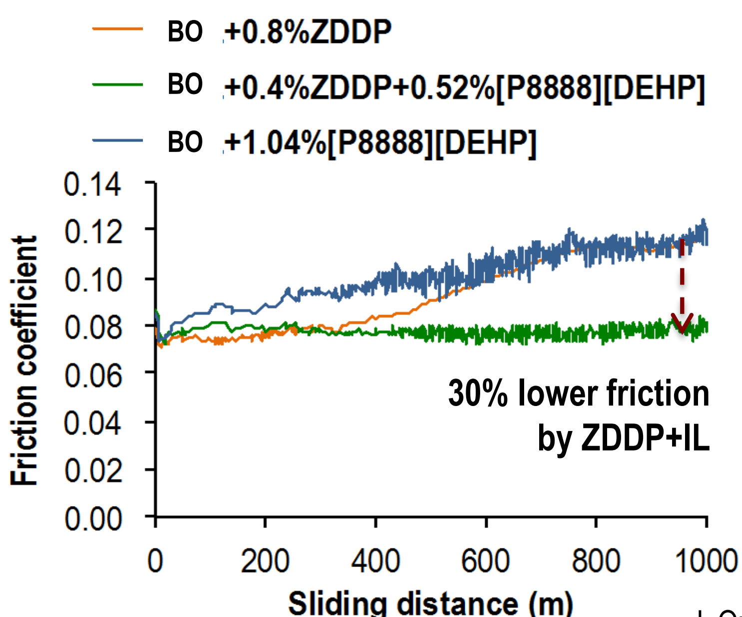


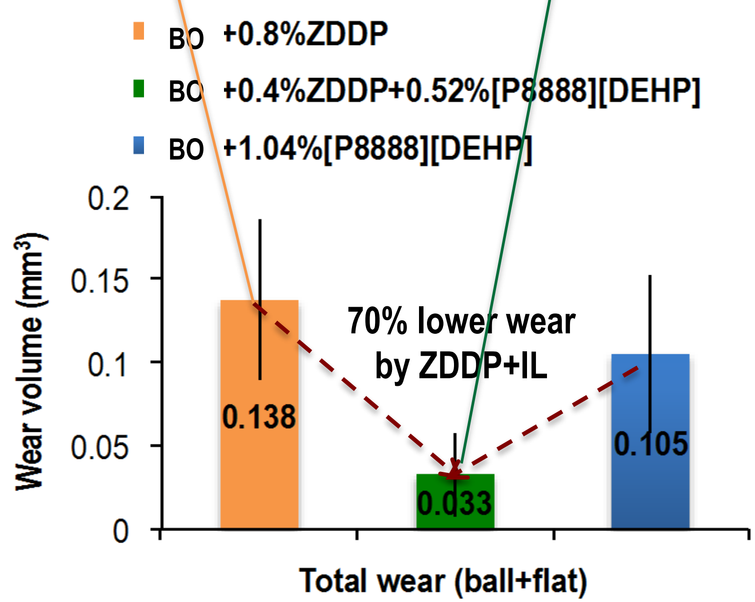


Synergistic effects discovered between $[P_{8888}][DEHP]$ and ZDDP (FY 2014)









J. Qu, et al., ***Advanced Materials*** 27 (2015) 4767.

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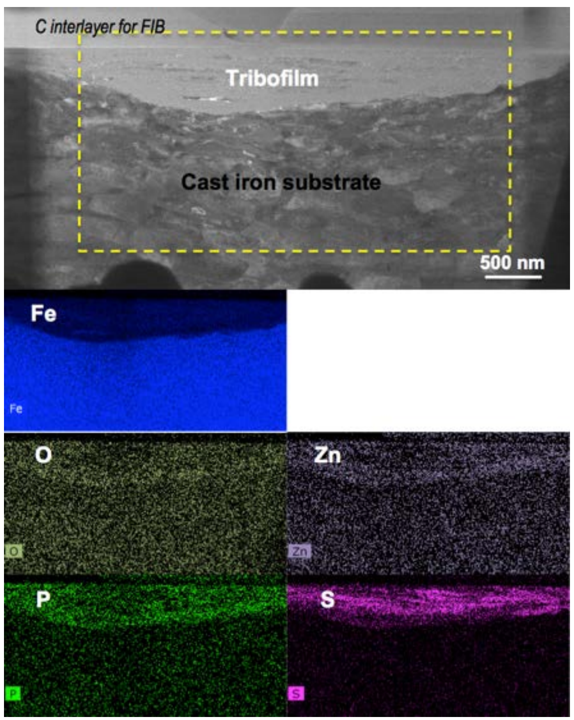
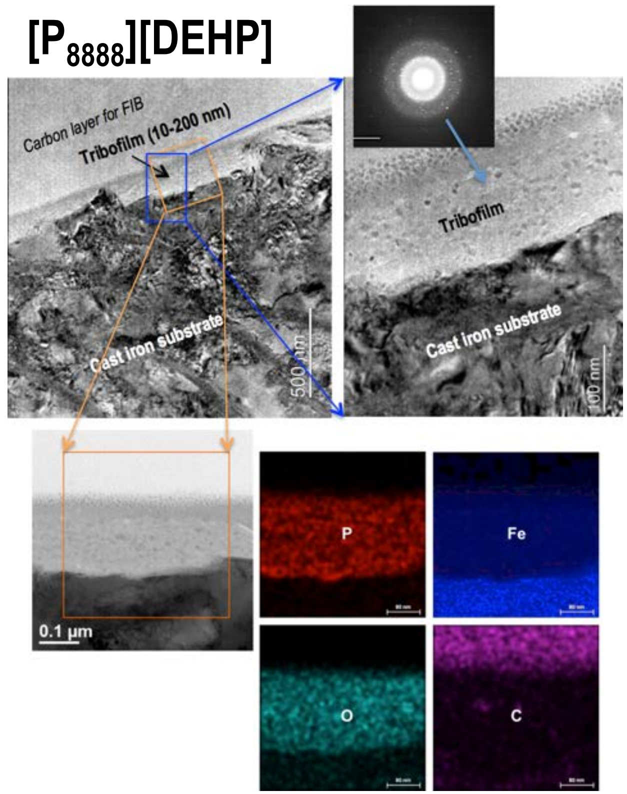
FY 2015 to understand the mechanisms – similar tribofilm morphology, *but…*

- **FIB-aided TEM/EDS of ZDDP, IL, and ZDDP+IL tribofilms**
  - **Similarity: thickness: 10-400 nm, amorphous matrix embedded with some nanocrystals**
  - **Difference: IL+ZDDP tribofilm seems to contain little S but more Zn compared with ZDDP tribofilm…**

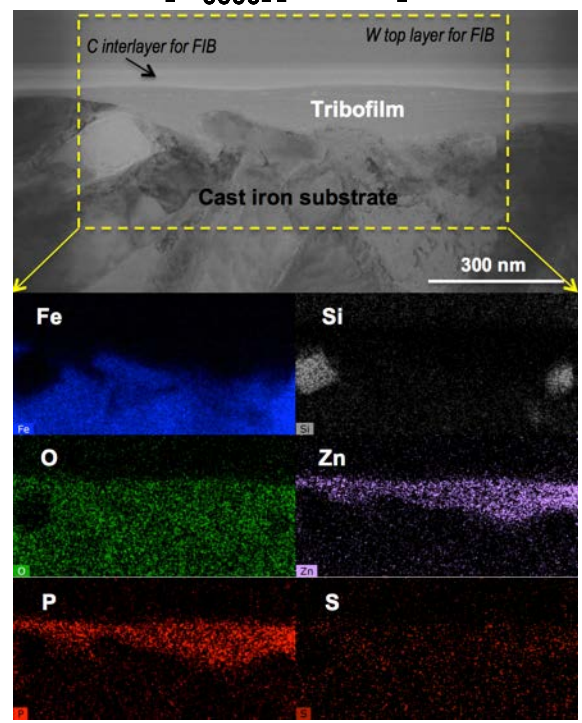
ZDDP



$[P_{8888}][DEHP]$



$ZDDP+[P_{8888}][DEHP]$



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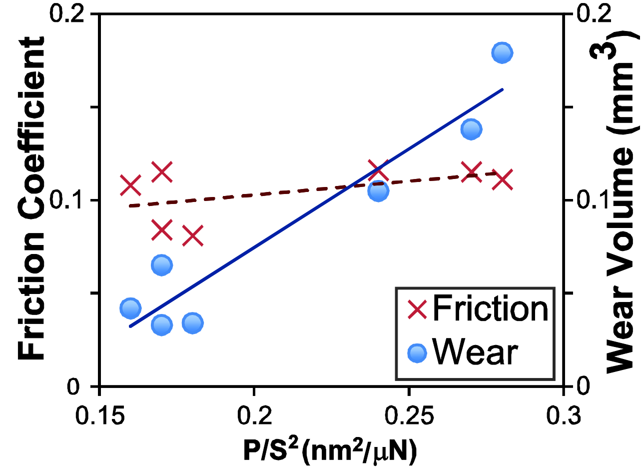
Change of tribofilm composition correlates well with mechanical properties

- Tribofilms by synergistic IL+ZDDP combinations contain more Zn and Fe phosphates than oxides
  - Much increased Zn compounds, but almost eliminated S contents compared with a ZDDP tribofilm;
- Lower hardness to stiffness squared (P/S^2) leading to reduced friction and wear
  - Opposite trend as reported for bulk or coating materials;
  - **Attributed to the sacrificial and self-healing nature of tribofilms.**

Nanoindentation of tribofilms



Ratio of hardness to stiffness squared

XPS	Element in tribofilm (at%)	C	Fe (metal)	Fe (ion)	O (oxide)	O (O-P)	P	S	Zn
BO	+0.8%ZDDP	6.7	0.7	13.3	11.1	42.8	10.3	8.4	6.5
	+1.04%[P_{8888}][DEHP]	7.0	1.2	16.3	25.1	39.3	11.1	0	0
	+0.4%ZDDP+0.52%[P_{8888}][DEHP]	**7.0**	**1.2**	**12.8**	**2.9**	**52.8**	**12.2**	**1.1**	**10.0**
	+1.0%[P_{66614}][BTMPP]	17.4	3.6	24.2	31.3	20.7	2.8	0	0
	+0.4%ZDDP+0.5%[P_{66614}][BTMPP]	8.0	14.7	21.7	39.3	12.8	1.3	1.7	0.4
	+1.74%[N_{888}H][DEHP]	14.2	15.9	10.8	22.2	28.9	8.0	0	0
	+0.4%ZDDP+0.87%[N_{888}H][DEHP]	12.3	5.7	22.7	12.8	36.5	7.1	1.7	1.2

J. Qu, et al., ***Advanced Materials*** 27 (2015) 4767; A.K. Landauer, W.C. Barnhill, J. Qu*, ***Wear*** 354 (2016) 78-82.

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Dramatically increased concentrations of active elements on oil surface: *responsible for synergism?*

Concentrations of P, S, O, and Zn 30-70X higher than nominal values on the oil droplet surface!

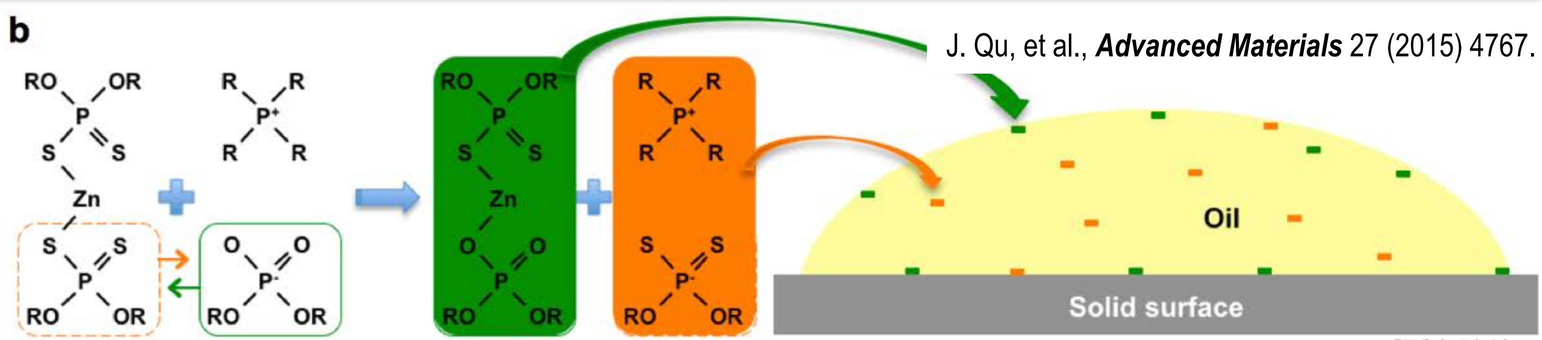
XPS

Base oil

Element concentration on oil surface (at%) (ratio of measured/nominal)	O	Zn	S	P
+0.8%ZDDP (nominal)	*0.0731*	*0.0183*	*0.0731*	*0.0365*
+0.8%ZDDP (measured)	0.125 (1.7x)	0.035 (1.9x)	0.11 (1.5x)	0.06 (1.6x)
+1.04%[P_{8888}][DEHP] (nominal)	*0.0728*	*0*	*0*	*0.0364*
+1.04%[P_{8888}][DEHP] (measured)	0.143 (2.0x)	0	0	0.06 (1.6x)
+0.4%ZDDP+0.52%[P_{8888}][DEHP] (nominal)	*0.0730*	*0.0091*	*0.0365*	*0.0365*
+0.4%ZDDP+0.52%[P_{8888}][DEHP] (measured)	**4.40 (60x)**	**0.68 (74x)**	**1.19 (33x)**	**1.19 (33x)**
+0.4%ZDDP+0.52%[P_{66614}][DEHP] (measured)	**2.89 (40x)**	**0.55 (60x)**	**1.09 (30x)**	**1.11 (30x)**
+0.4%ZDDP+0.5%[P_{66614}][BTMPP] (measured)	0.20 (3.7x)	0.05 (5.5x)	0.10 (2.8x)	0.09 (2.5x)
+0.4%ZDDP+0.87%[N_{888}H][DEHP] (measured)	0.24 (2.0x)	0.03 (4.9x)	0.04 (1.6x)	0.05 (1.4x)

Atomic ratio of O:Zn:S:P close to 3:0.5:1:1, suggesting anion exchange between IL and ZDDP?

Anion exchange favorable based on the chemical hardness principle



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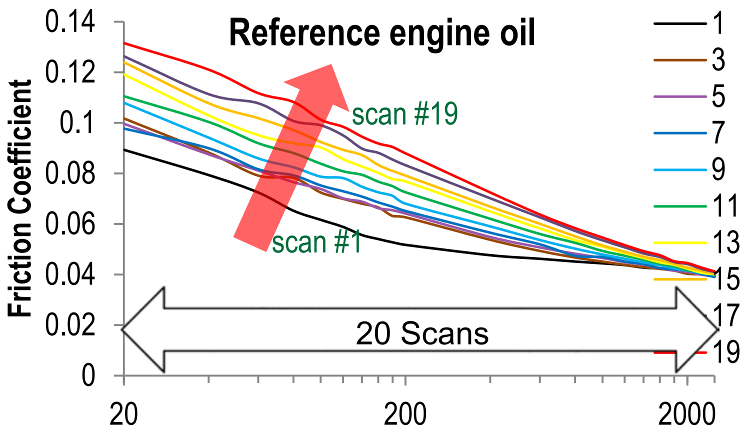
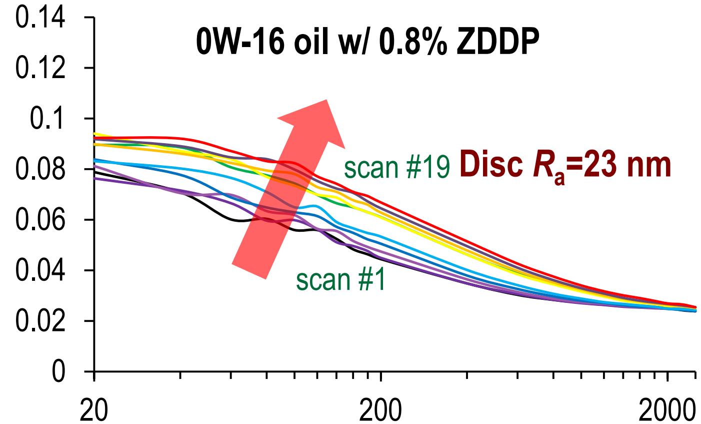
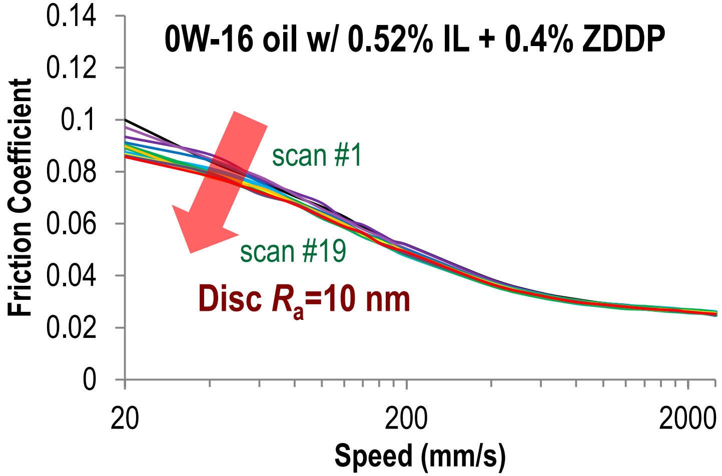
Prototype IL+ZDDP additized SAE 0W-16 engine oil produces lower boundary and mixed friction in bench tests (Shell data)

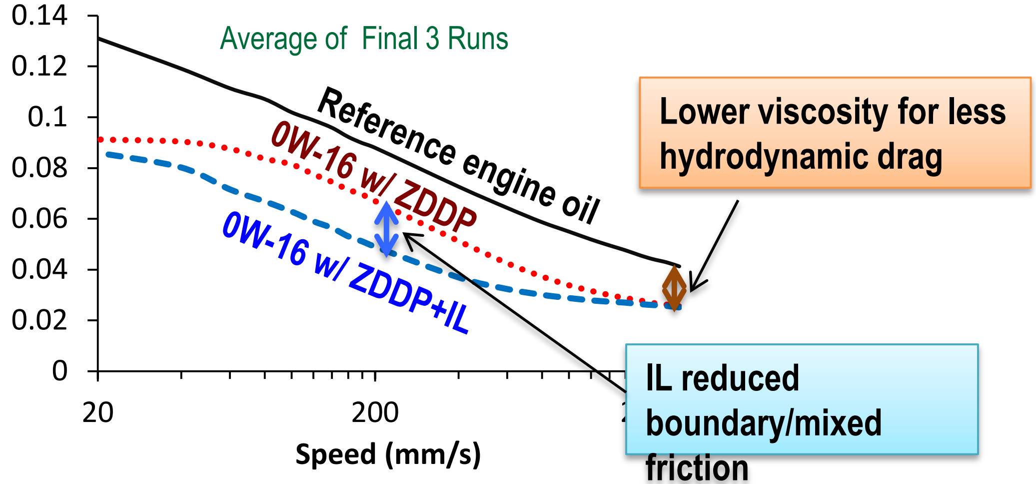
- **Two experimental SAE 0W-16 engine oils w/ different AWs: (a) ZDDP only and (b) ZDDP+[P_{8888}][DEHP] with the same nominal P concentration of <800 ppm (meeting ILSAC GF-5/6 specs).**





- 30 N load
- 100 ºC
- Slide-roll ratio: 100%





W.C. Barnhill and J. Qu*, et al., ***Frontiers in Mechanical Engineering***, 1 (2015) 12.

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Prototype IL+ZDDP additized SAE 0W-16 engine oil demonstrated improved fuel economy in engine dyno tests

Sequence VIE (ASTM D7589) FEI 1 fuel economy engine dyno tests at InterTek

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Engine condition	2000 rpm, 105 N-m, 115 °C	2000 rpm, 105 N-m, 65 °C	1500 rpm, 105 N-m, 115 °C	695 rpm, 20 N-m, 115 °C	695 rpm, 20 N-m, 35 °C	695 rpm, 40 N-m, 115 °C
Lubrication regime	**Dominated by HD/EHD lubrication**			**More boundary & mixed lubrication**		
0W-16 w/ ZDDP vs. BLB	**2.36%**	**2.84%**	**1.66%**	**3.72%**	**5.98%**	**3.03%**
0W-16 w/ ZDDP+IL vs. BLB	**2.54%**	**2.91%**	**1.77%**	**4.48%**	**6.46%**	**3.81%**
ZDDP+IL vs. ZDDP only	**0.17%**	**0.07%**	**0.11%**	**0.76%**	**0.48%**	**0.79%**

1.77 – 6.46% FEI for the prototype IL+ZDDP additized engine oil

1.66 – 5.98% FEI by using lower viscosity oil (0W-16) to reduce HD/EHD drag

0.07 – 0.79% FEI by using IL+ZDDP to reduce boundary/mixed friction vs. ZDDP only

Synergistic IL+ZDDP offers opportunities in mitigating increased wear and boundary friction for the trend of using lower-viscosity oils and highly-boosted low-speed downsized engines.

W.C. Barnhill and J. Qu*, et al., ***Frontiers in Mechanical Engineering***, 1 (2015) 12.

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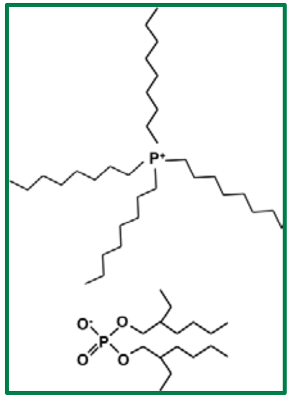
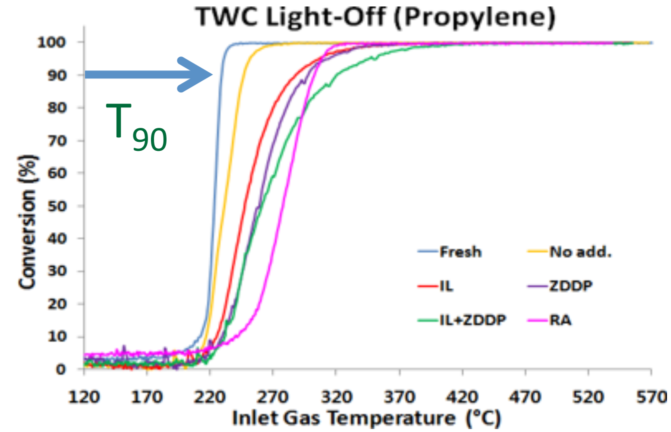
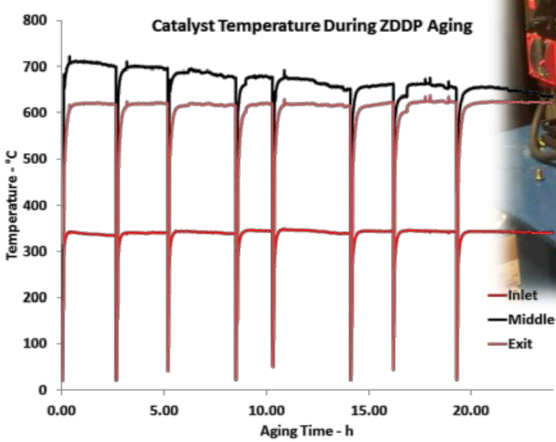
Approach – Lubricant effects on emissions control technologies (AOP Task-1)

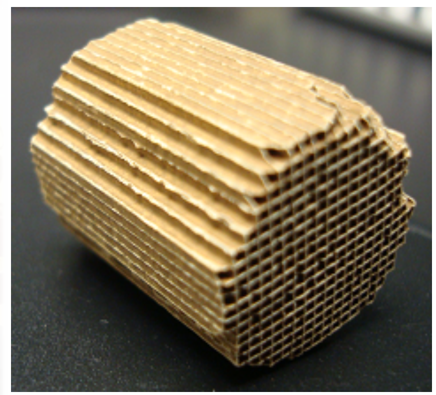
1. Add lubricant-additive to fuel in quantity that reflects lifetime exposure

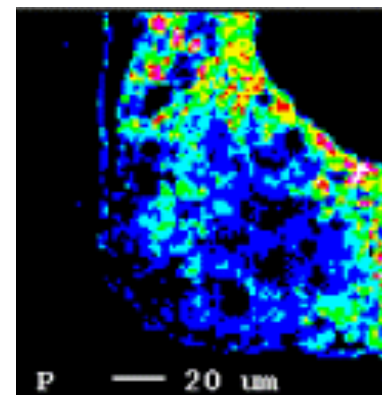
2. Using gasoline genset, operate at relevant exhaust conditions with commercial TWC











3. Core aged-TWC samples for bench flow reactor evaluation

4. Characterize aged-TWCs for chemical and material properties; compare to standards

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Evaluated compatibility of full range of lubricant additives with TWCs

- **Baseline TWC is from a MY2009 Jeep Liberty V6**
  - Obtained TWCs from local dealership
  - Also have baseline aged-TWC from ethanol intermediate blend study
    - gasoline fuel, 116k miles driven on the road-cycle

- **TWCs evaluated in study**
  - Fresh: as-received TWC
  - NA: No-additive baseline
  - IL: ionic liquid lubricant-additive
  - ZDDP: industry standard
  - IL+ZDDP: best lubricant formulation
  - FUL: TWC aged to full-useful life on the road-cycle

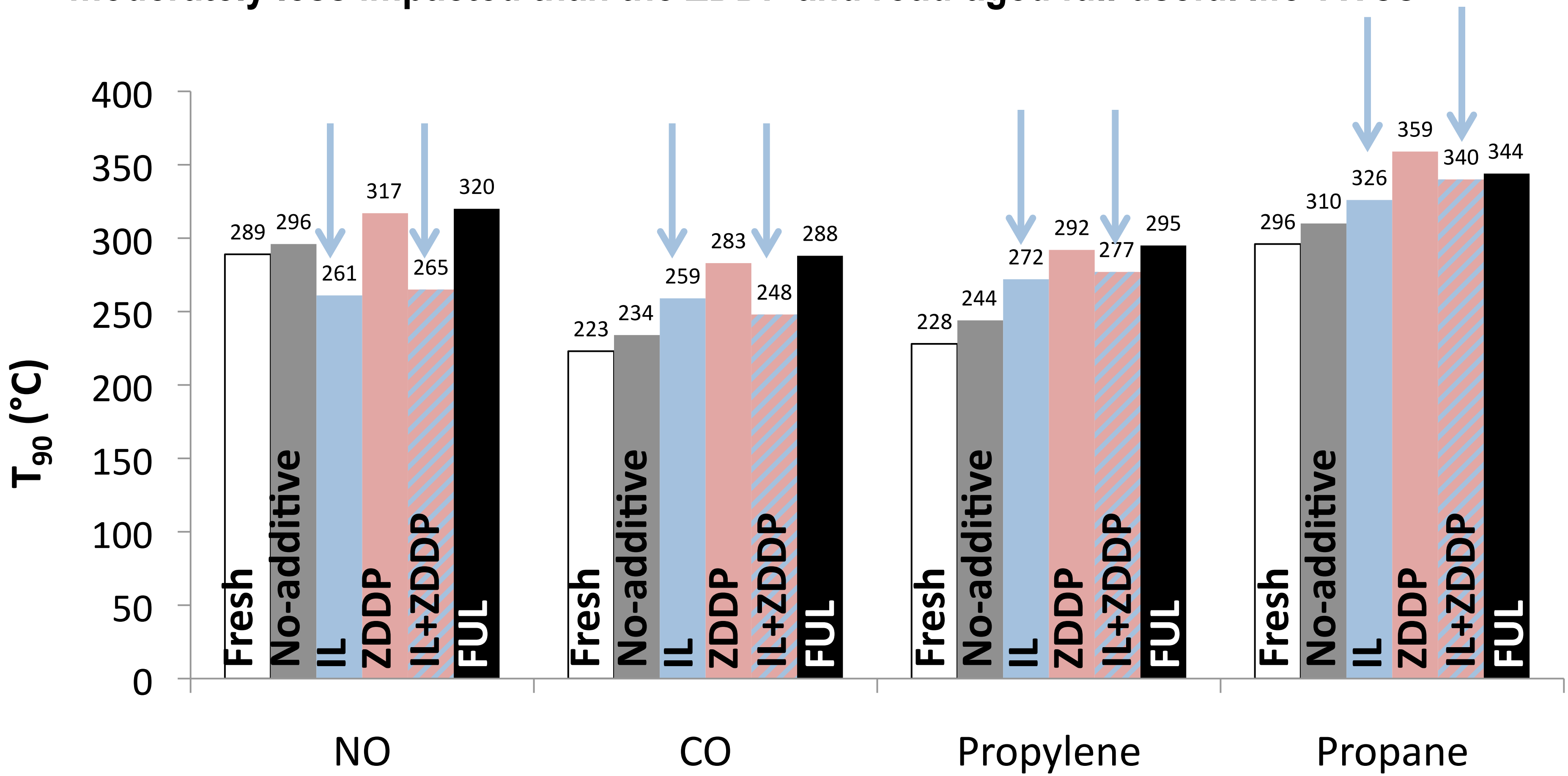
- **Evaluated directly after aging and following desulfation, de-sooting steps**

- **Evaluation conditions**

Gas	Concentration
Propylene	850 ppm
Propane	100 ppm
CO	0.5%
NO	0.1%
O_2	0.4-0.8%
H_2	0.167%
H_2O and CO_2	13%
GHSV	60k h^{-1}

IL generally has moderately less catalytic impact than ZDDP

- **After removing any residual sulfur and soot, all of the IL-containing TWCs are moderately less impacted than the ZDDP and road-aged full-useful life TWCs**



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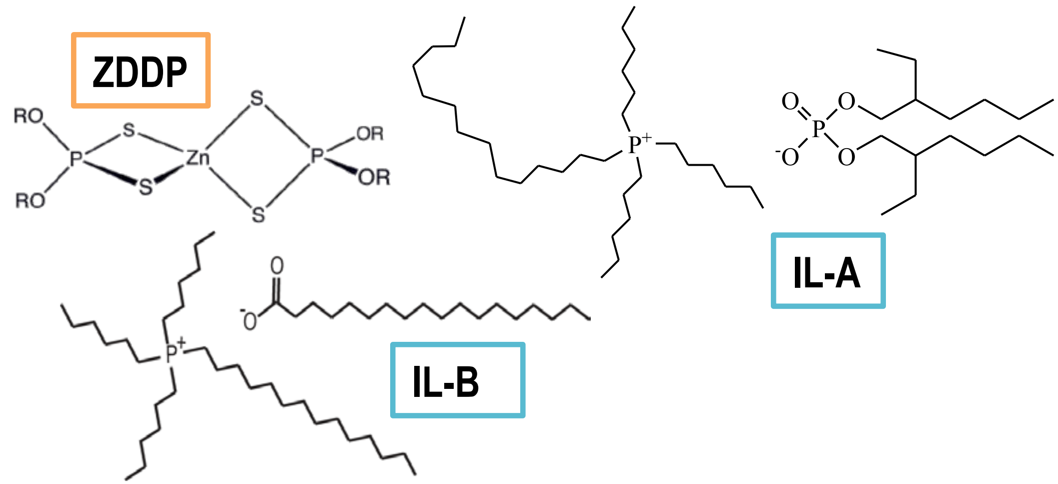
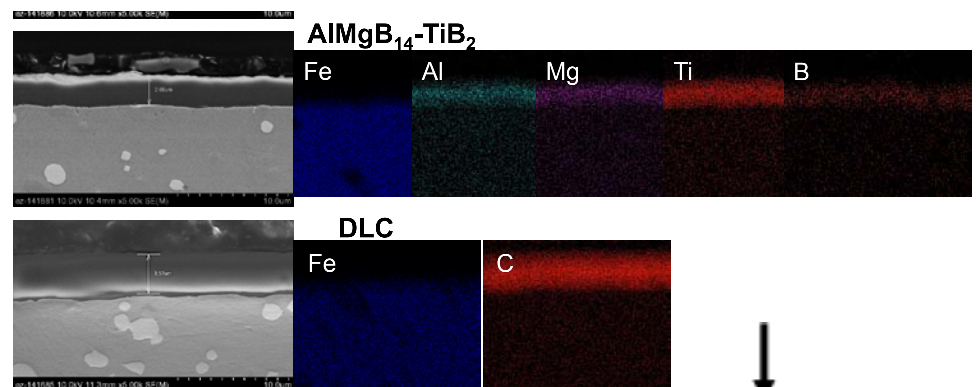
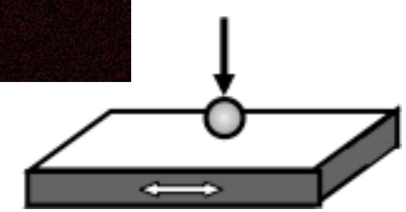
Approach – Compatibility of lubricant anti-wear additives with hard coatings (AOP Task-2)

- **Lubricants**
  - SAE 0W-30 base oil (Chevron) + AW
  - ZDDP (secondary, Lubrizol)
  - IL-A ([P_{66614}][DEHP])
  - IL-B ([P_{66614}][$C_{17}H_{35}COO$])
- **Coatings (PVD)**
  - Diamond-like-carbon (DLC, a-CH)
  - DLC (ta-C)
  - $AlMgB_{14}$+50 vol%TiB_2 (BAM)
- **Friction and wear testing**
  - Ball-on-flat reciprocating sliding: 52100 steel ball against coatings (100 N, 10 Hz w/ 10 mm stroke, 1000 m, 100 °C)
- **Mechanistic investigation via tribofilm characterization**
  - SEM, TEM/EDS, and XPS



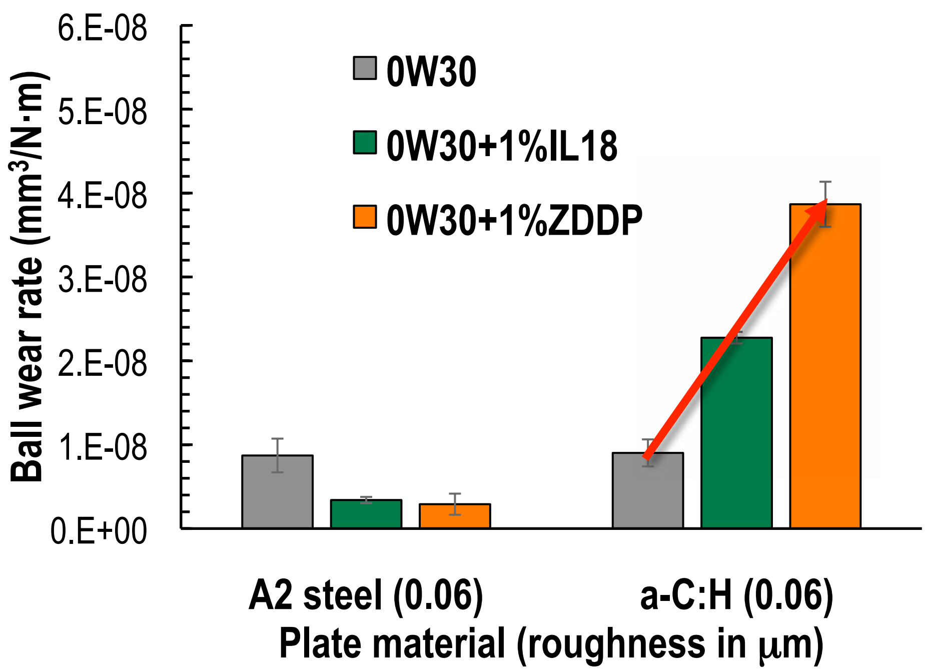


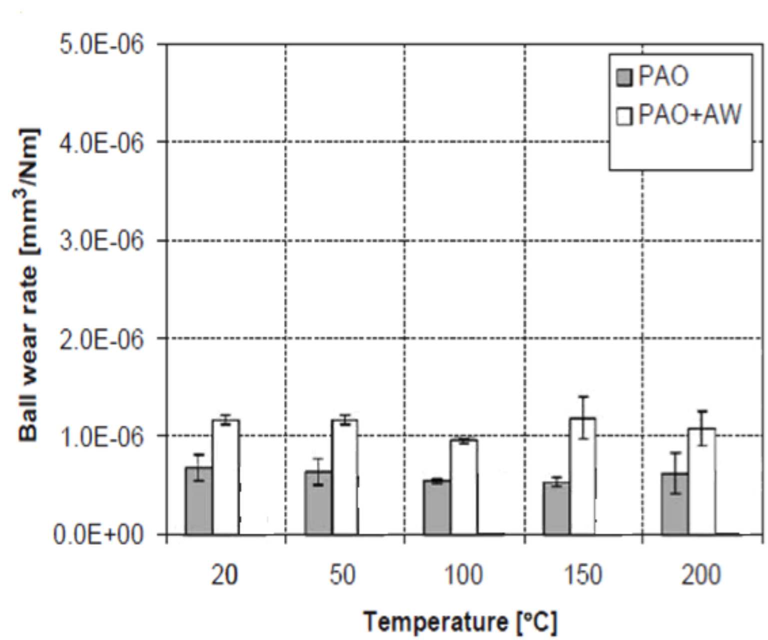


Oak Ridge National Laboratory

Steel ball experienced higher wear when rubbing against DLC in presence of ZDDP or phosphate IL (FY 2014)

- **Using DLC and ZDDP together actually increased the steel ball wear (by ~4X compared with using neither) instead of simply competing each other…**
  - **The wear of the steel counterface against DLC was largely ignored in the literature, except** [*Spikes, Tribol Int 2011*] **and** [*Podgornik, Surf Coat Tech 2005*] **that had similar observations!**
- **Using DLC and [P_{66614}][DEHP] together also increased the steel ball wear, but less bad (~2X)...**

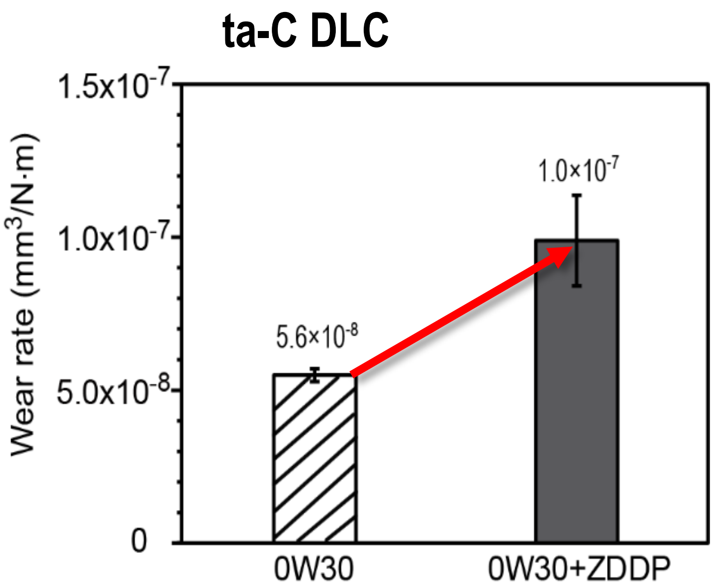


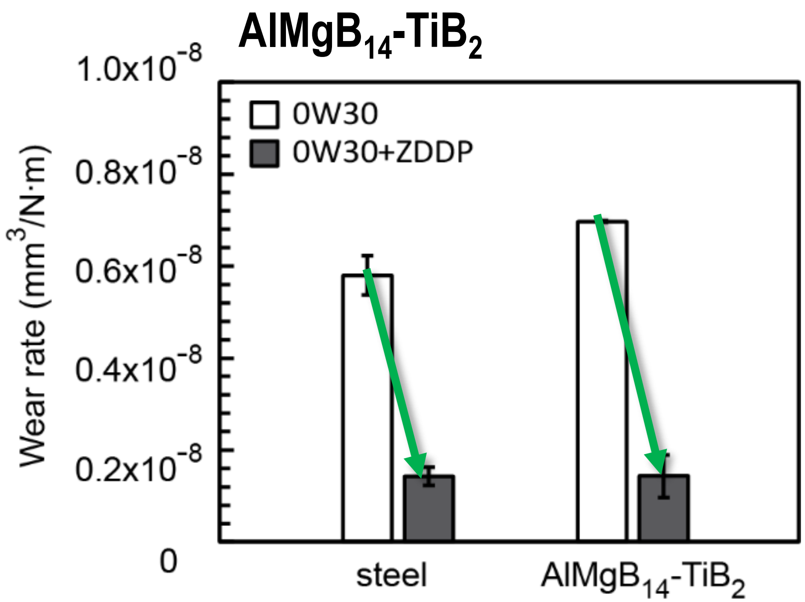


Y. Zhou and J. Qu*, et al., ***Advanced Materials Interfaces*** 2 (2015) DOI: 10.1002/admi.201500213.

FY 2015: Investigating the mechanism behind the antagonistic effect

Applicable to other coatings?



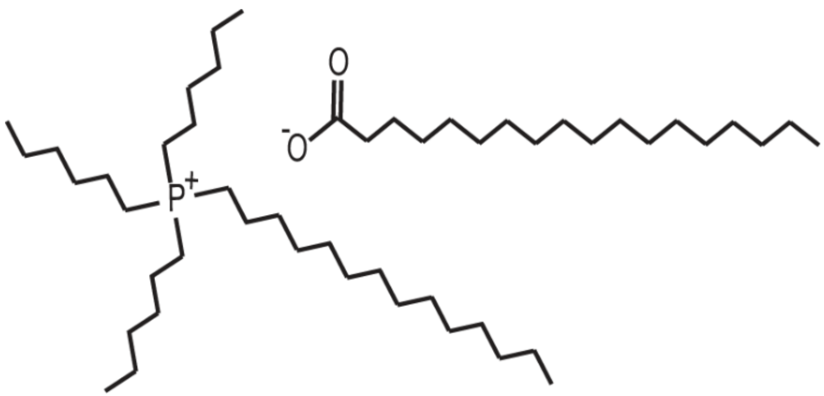


- **H-free ta-C also increased the steel ball wear;**
- **C-free $AlMgB_{14}$-TiB_2 did not increase ball wear;**

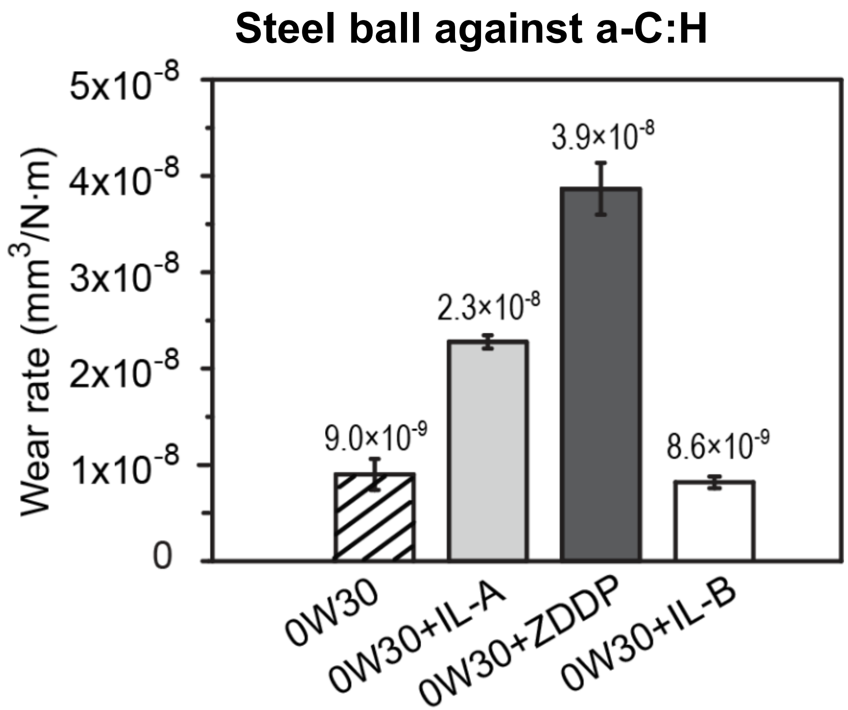
Carbon (from DLC) seems the cause from the material side…

Y. Zhou and J. Qu*, et al., ***Advanced Materials Interfaces*** 2 (2015) DOI: 10.1002/admi.201500213.

Applicable to other ILs?



IL-B: $[P_{66614}][C_{17}H_{35}COO]$



Phosphate anion seems the cause from the chemical side…

	Phosphate (wt%)
BO+1%ZDDP	10
BO+1%IL-A	3.9
BO+1%IL-B	0

Y. Zhou and J. Qu*, et al., ***Advanced Materials Interfaces*** 2 (2015) DOI: 10.1002/admi.201500213.

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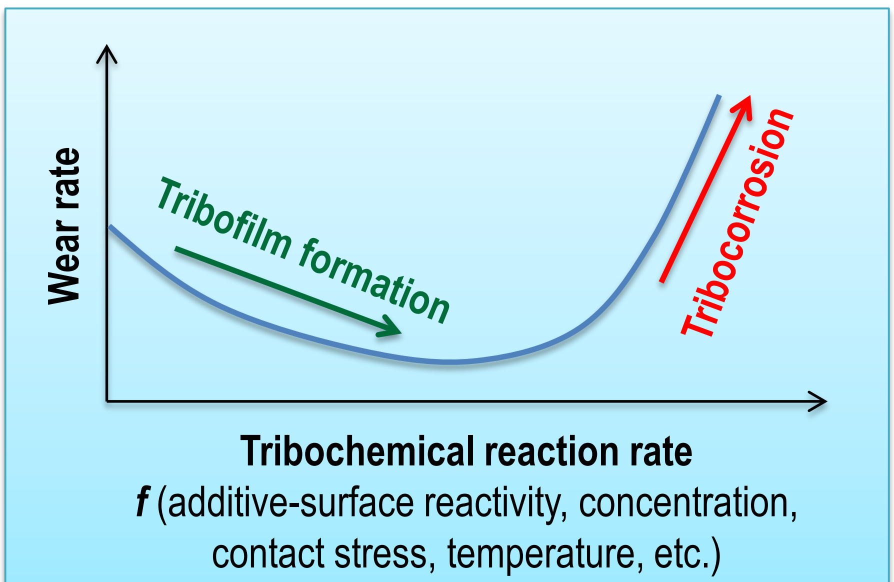
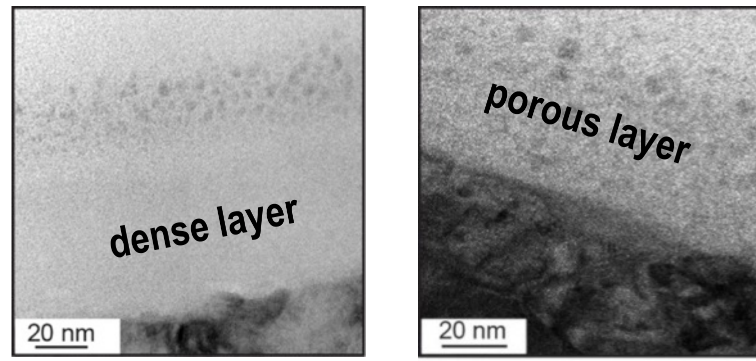
Hypothesis

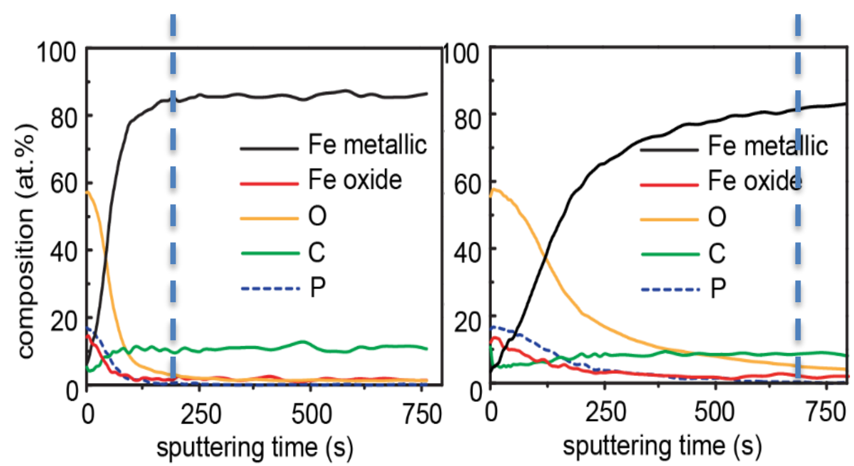
- It is known that an anti-wear additive with reactivity unnecessarily high may cause higher wear rate [*Chem & Tech Lubricants*, 2011]
- **sp^2 and sp^3 carbon from DLC are good catalysts, which may accelerate the chemical reactions between phosphate anions and steel surface, and change the protective tribofilm formation process to detrimental tribocorrosion!**



A thicker and porous tribofilm found on the ball against DLC, supporting the tribocorrosion hypothesis…

ball against steel **ball against a-C:H**





Y. Zhou and J. Qu*, et al., ***Advanced Materials Interfaces*** 2 (2015) DOI: 10.1002/admi.201500213.

Responses to Previous Year Reviewers' Comments

- **Not applicable – this project was not reviewed last year.**

Collaboration

- FOA/CRADA partner: Shell Global Solutions (US)
  - Participated in tribological bench testing
  - Conducted industrial standard no-harm storage, corrosion, and elastomer compatibility tests of candidate ILs
  - Led engine oil formulation
  - Produced prototypes of IL-additized low-viscosity engine oils
- Other collaborators:
  - Cytec Industries: supplied feed stocks to ORNL for synthesizing ILs
  - Chevron: supplied base oil
  - Lubrizol: supplied ZDDP
  - NCT, IonBond, Eaton, Hardcoat, and ANL: provided various coatings
  - UT: hosted graduate students
  - PSU: chemical analysis of oil-solid interfaces using total reflection infrared (ATR-IR) spectroscopy (subcontract)

Remaining Challenges and Barriers

- ILs' molecular structures remain to be optimized.
- IL's oil miscibility theory is not fully established yet.
- IL+ZDDP lubricating mechanism is not fully understood yet.
- Compatibility of ILs with friction modifiers, detergents, and dispersants requires further investigation.
- Performance of ILs in aged engine oil containing water, fuels, and soot is little known.
- ILs' lubricating functionality for other vehicle bearing components, such as rear axle, is yet to be studied.
- ILs' compatibility with non-ferrous bearing materials, such as bronze and Al-Si alloys (used for connecting rod end bushings/bearings), are to be studied.
- Are the materials difference in the IL+ZDDP TWCs consistent with ZDDP or IL? Neither?

Summary

- **Accomplishments in FY 2015-16:**
  - Successfully completed the joint FOA project with Shell.
  - Identified a specific IL group with unique synergistic with ZDDP and gained mechanistic understanding of the synergism.
  - Investigated compatibility between a candidate IL and other oil additives and produced a prototype low-viscosity (SAE 0W-16) fully-formulated engine oil.
  - Conducted Sequence VIE engine dyno tests to demonstrated FE improvement for the IL+ZDDP additized prototype engine oil, and was able to separate the contributions from the lower viscosity and friction reduction.
  - Studies the impact of IL, ZDDP, and IL+ZDDP on TWC using accelerated engine tests and results suggested less adverse impact of IL than ZDDP.
  - Gained fundamental understanding of the antagonistic effect when using phosphate AW with DLC coatings.
- **Future Work:**
  - Further develop the IL technology for both engine and rear axle lubrication to get a combined FEI in a new joint FOA project with GM.
  - Investigate the impact of new ILs and IL+ZDDP combinations on TWC.
  - Understand the compatibility of ILs and IL+ZDDP combinations with bronze and aluminum bearing alloys.

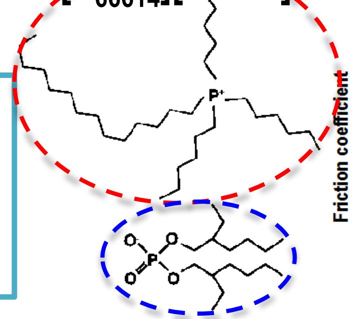
Technical Back-up Slides

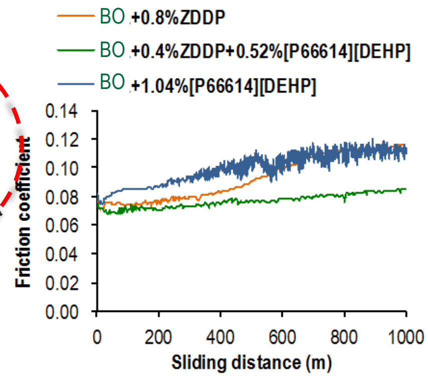
Synergism with ZDDP observed for *but only for* phosphonium-alkylphosphate ILs

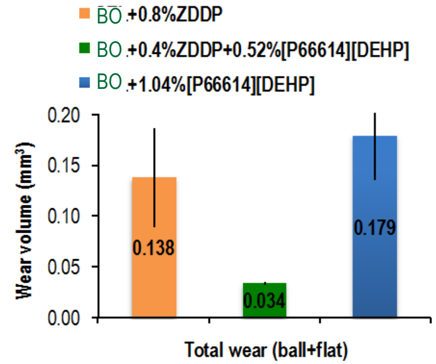
Phosphonium-alkylphosphate $[P_{66614}][DEHP]$

ZDDP only, IL only, and IL+ZDDP (total P of 800 ppm).

Equal P (400 ppm) from IL and ZDDP for each combination.

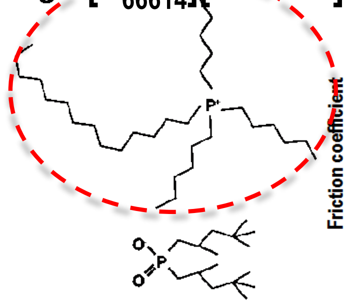


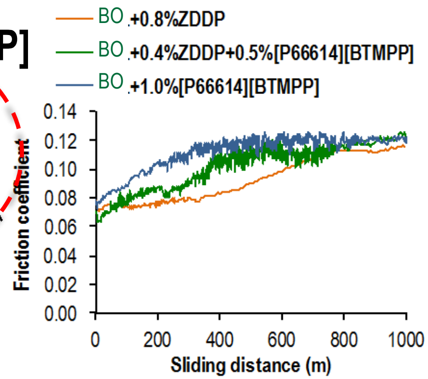


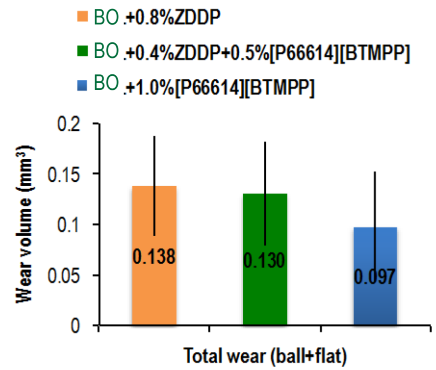


Phosphonium-alkylphosphinate $[P_{66614}][BTMPP]$

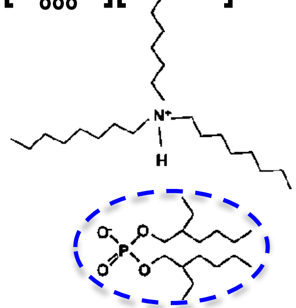
Both the cation and anion play critical roles on the IL+ZDDP synergy!

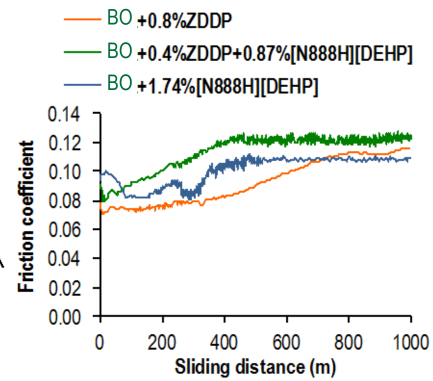


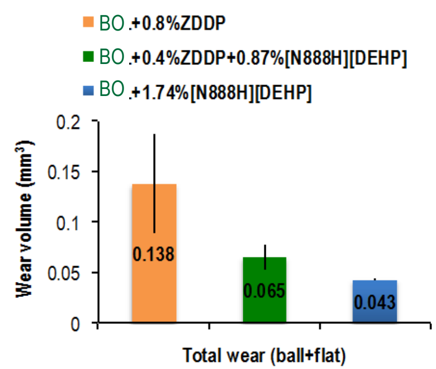




Ammonium-alkylphosphate $[N_{888}H][DEHP]$



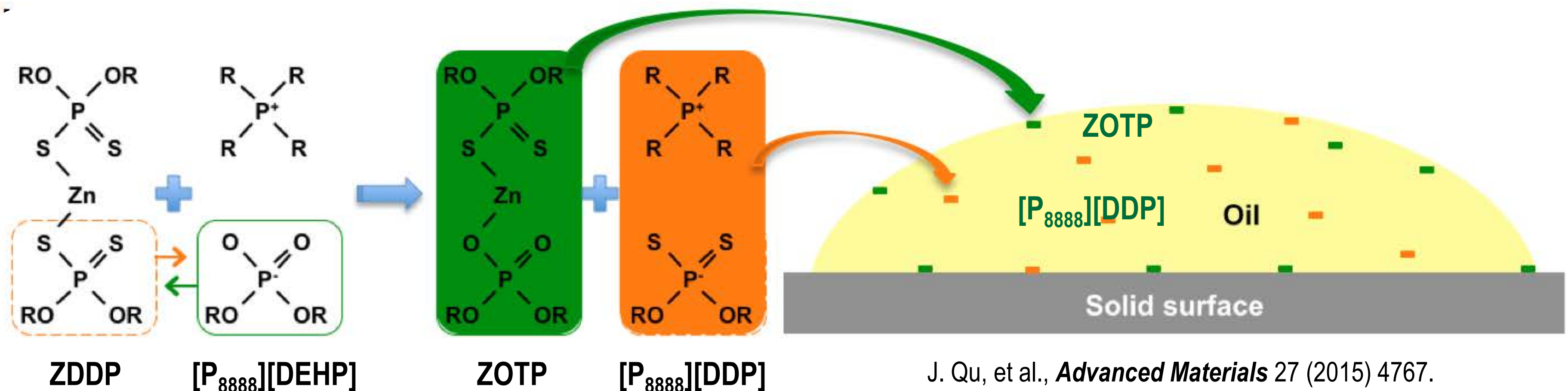




J. Qu, et al., ***Advanced Materials*** 27 (2015) 4767.

Hypothesis: new compounds formed by anion exchange between IL and ZDDP

- **Anion exchange favorable based on the chemical hardness principle**
  - **$[P_{8888}]^+$ is a harder Lewis acid compared with the Zn^{2+} (a neutral organic more difficult to lose electrons than a neutral metal, thus a softer base);**
  - **$[DEHP]^-$ is a softer Lewis base than DDP^- (O^0 is stronger acid than S^0)**
- **For ZDDP + $[P_{8888}]$[DEHP] at 1:1 molecular ratio, ultimately each ZDDP would have one DDP^- replaced with [DEHP]:**
  - **ZDDP + $[P_{8888}]$[DEHP] → ZOTP + $[P_{8888}]$[DDP]**
- **The measured ratio of O:Zn:S:P (3.7:0.57:1:1) on the oil surface of BO+ZDDP+$[P_{8888}]$[DEHP] is similar to the nominal atomic ratio 3:0.5:1:1 of ZOTP!**



J. Qu, et al., ***Advanced Materials*** 27 (2015) 4767.

Formulation of the prototype IL+ZDDP additized SAE 0W-16 engine oil

Table 1. Formulation

Lubricant	Detergent-A	Dispersant-B	Viscosity Modifier	Anti-oxidant	Friction Modifier	Pour-point depressant	Anti-foam	Anti-wear	
								ZDDP	$[P_{8888}]$[DEHP]
0.8% ZDDP	3%	2%	2.4%	1%	0.8%	0.3%	0.03%	0.8%	0%
0.52% IL + 0.4% ZDDP	3%	2%	2.4%	1%	0.8%	0.3%	0.03%	0.4%	0.52%

Table 2. Physiochemical properties

Lubricant	Density (g/cm^3)	P Content (ppm)	Zn Content (ppm)	Viscosity Index	HTHS @ 150 °C (cP)	Kinematic Viscosity (cSt)	
						40°C	100°C
0.8% ZDDP	0.84	723	836	157	2.4	38.5	7.3
0.52% IL + 0.4% ZDDP	0.84	705	392	155	2.4	38.8	7.3

SAE 0W-16

W.C. Barnhill and J. Qu*, et al., ***Frontiers in Mechanical Engineering***, 1 (2015) 12.

Performance evaluation of fresh and aged TWC samples

- **Degreening**
  Middle of catalyst temperature at 700°C for four hours in 10% H_2O, 10% CO_2, and N_2 balance (only for fresh TWC)

- **Light-off Temperatures**
  Determining light-off temperature for NO, CO, and HCs under stoichiometric condition with simulated exhaust gases consisting of 850 ppm C_3H_6, 100 ppm C_3H_8, 0.5% CO, 0.1% NO, 0.167% H_2, 0.72% O_2, 13% H_2O, 13% CO_2, and N_2 balance
  - Temperature ramp: 100-600°C @ 5°C/min
  - Natural cooling : 5 minutes after temperature ramp the catalyst is cooled from 600°C to 150°C
  - Obtaining 1st light-off for fresh TWC sample and 2nd light-off for aged TWC samples

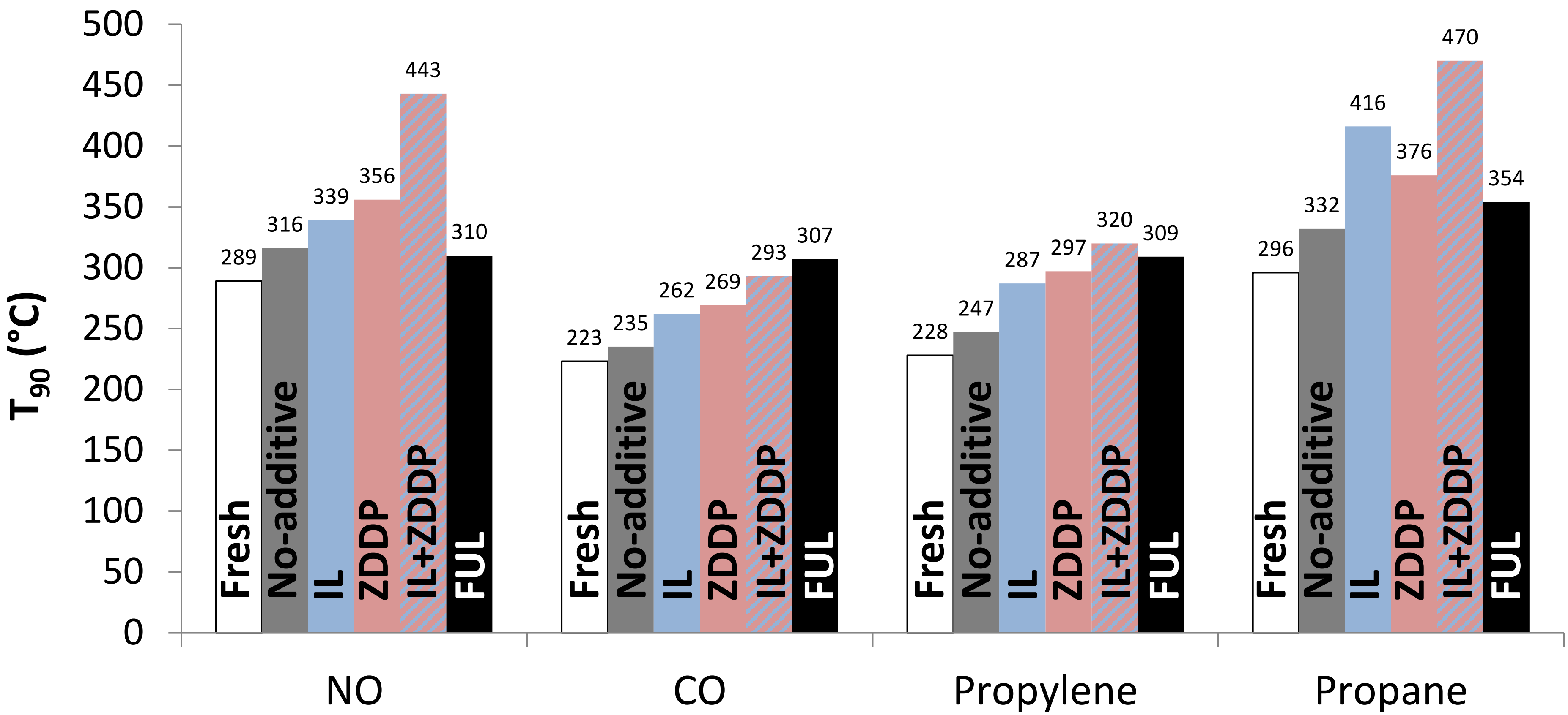
- **Water-gas shift reaction**
  - 0.5% CO, 13% H_2O, and N_2 balance
  - 200-550°C in 50°C increments

- **O_2 Storage**
  - Cycling between lean (0.69% O_2 and N_2 balance) and rich (0.5% CO and N_2 balance)
  - Cycling consists of 2 minutes lean followed by 2 minutes rich for four cycles for a total of 16 minutes
  - Varying temperatures from 300 to 550°C in 50°C increments

- **Desulfation/Desooting**
  -Cycling between lean (0.3% O_2, 0.2% H_2, 13% H_2O and N_2 balance) and rich (0.3% O_2, 1% CO, 13% H_2O and N_2 balance)
  -Cycling consists of 2 minutes lean followed by 2minutes rich for 30 cycles for a total of 2 hours
  - Maintaining temperature at middle of catalyst at 700 °C

IL generally has moderately less catalytic impact than ZDDP

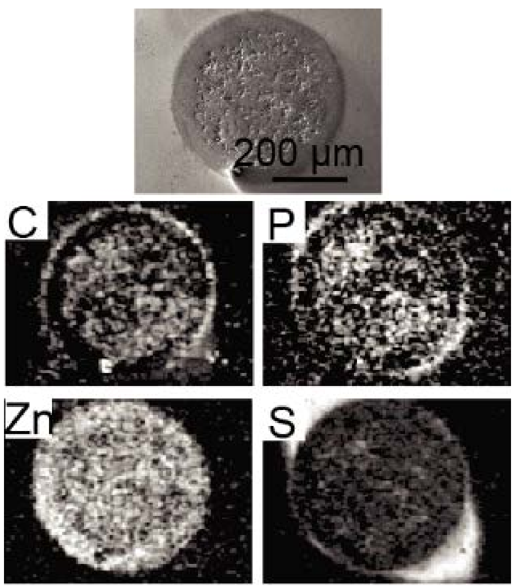
- **Before desulfation/de-sooting the IL+ZDDP has the highest T50 and T90, and thus appears to be the most impacted; after removing soot and sulfur trend is reversed**



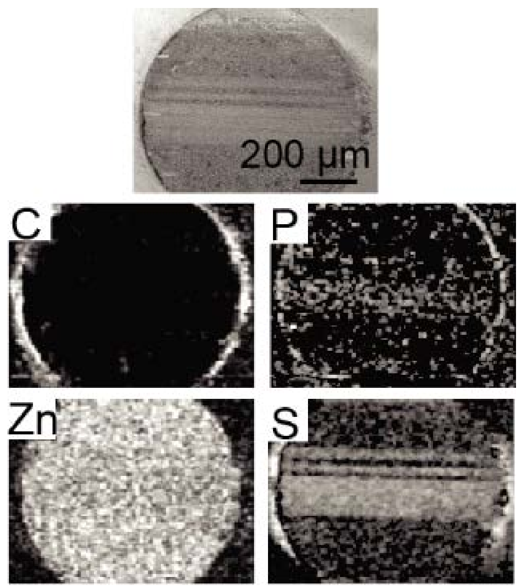
Earlier hypotheses for antagonistic effects between ZDDP and DLC

1. DLC carbon transfer competes with ZDDP tribofilm formation on steel ball surface to reduce the anti-wear effectiveness [*Spikes, Tribol Int 2011*]

- ***However, this cannot explain:***
  - **The significantly increased ball wear, much higher than that w/o using ZDDP nor DLC**
  - **EDS elemental maps show little C on the ball scar against DLC, not supporting carbon transfer**



Steel ball against steel plate



Steel ball against DLC-coated plate

2. Chemical-mechanical polishing (CMP) effect

- ***But this cannot explain:***
  - **Not applicable to non-carbon coatings or non-phosphate additives**

Y. Zhou and J. Qu*, et al., ***Advanced Materials Interfaces*** 2 (2015) DOI: 10.1002/admi.201500213.