Advances in Multi-functional Nanocomposite Coatings for Demanding Automotive Applications*

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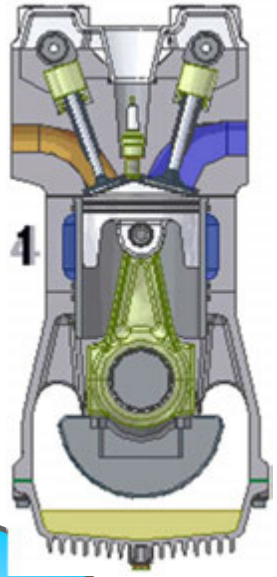
Outline of This Talk

- Brief overview of energy and environmental challenges in relation to automotive industry
- Advances in tribological coatings for automotive applications
- Design strategies for smart nano-composite coatings that are:
  - Catalytically active/reactive toward base oil compositions
  - Able to extract DLC-like boundary films in-situ from the base oils
- Fundamental mechanisms
- Summary

Current Engine Materials and Lubrication: New Realities/Challenges in Motored Vehicles



Cleaner Emissions:
Require Lower S and P (Low SAPS)

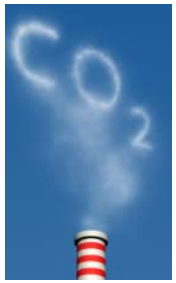
Often at odds with each other!

Longer Durability:
Call for increased use of ZDTP compounds – Increase S and P, Increase viscosity

Higher Fuel Economy:
More Use of MoDTC and Lower Viscosity Oils

- **Other Challenges:**
- Higher power density requirement
- Alternative (light-weight) engine materials (coatings)
- EGR and other after-treatment technologies

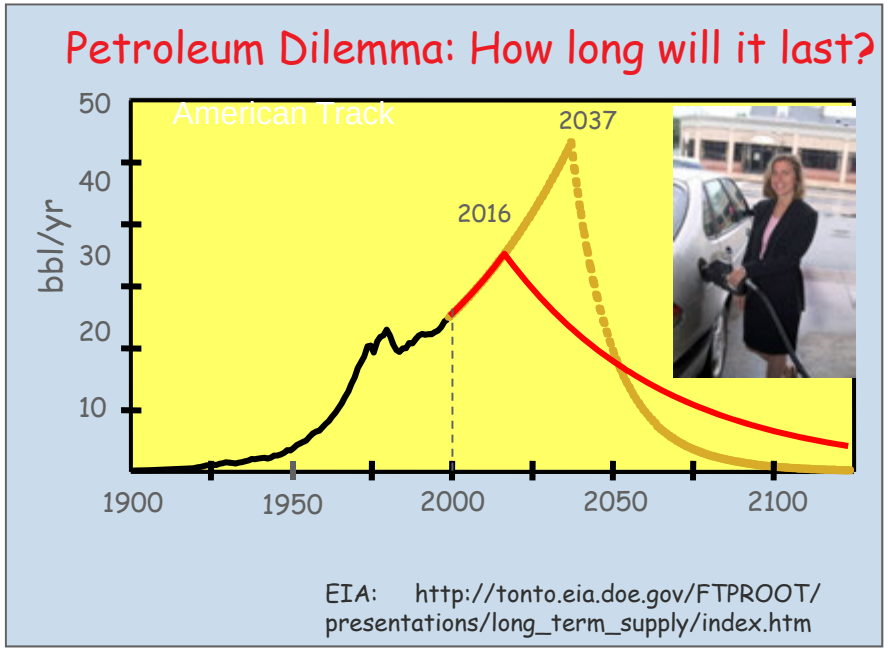
Impact of Friction on Energy & Environment

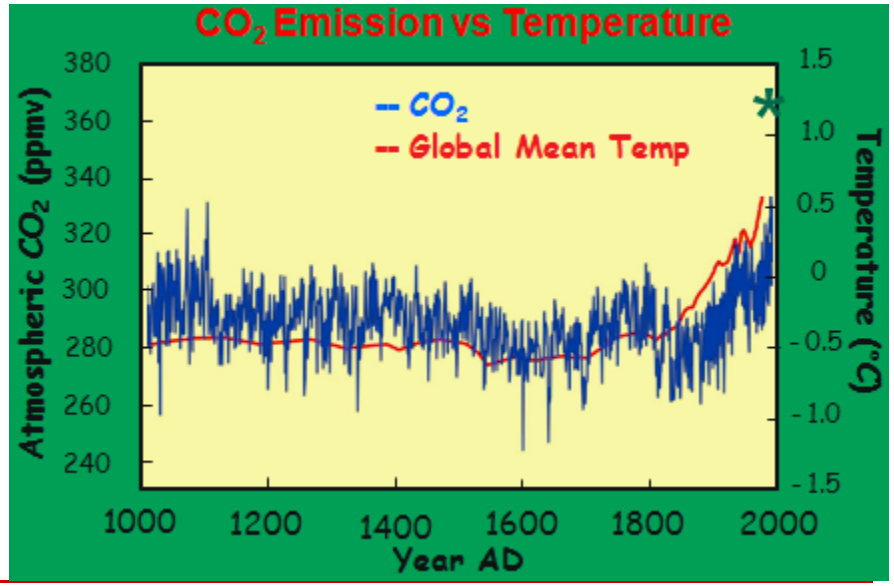


- **In highly industrialized nations, the annual cost of energy and materials losses due to friction and wear is estimated to be as much as 5% of their gross national products.**

- **Currently, there are about 800 million motored vehicles in our planet emitting 6B Tons CO_2/year.**

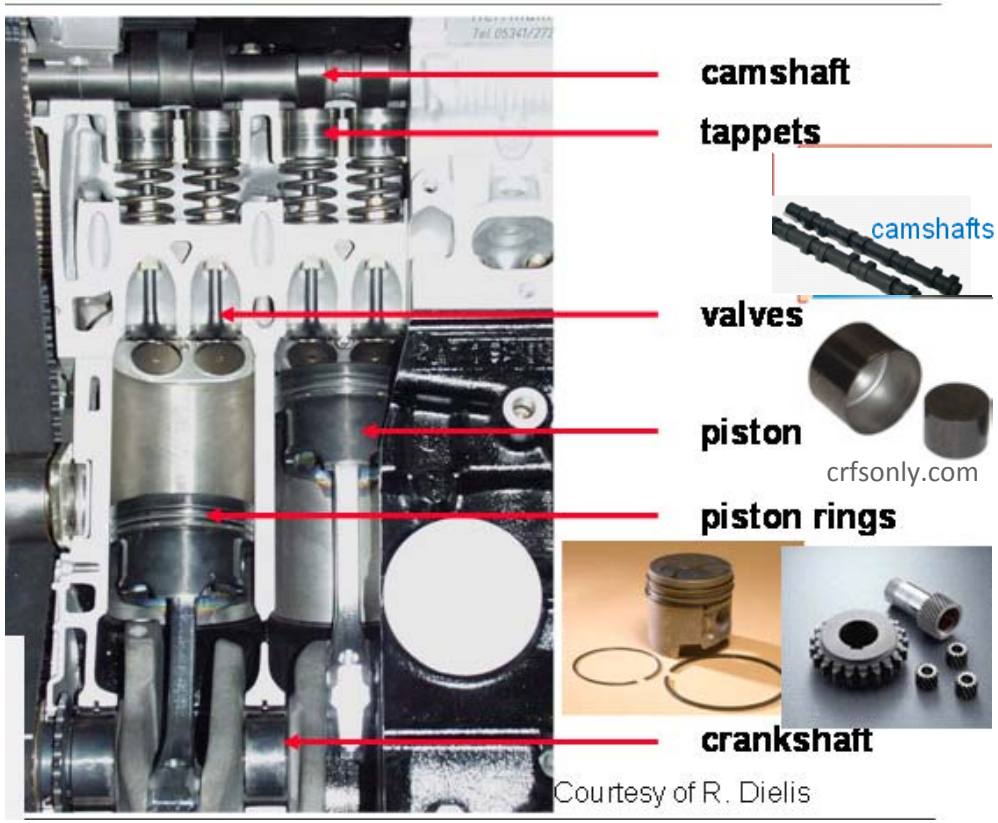
- **In these vehicles, high friction means high fuel consumption, and hence increased environmental pollution, greenhouse gasses, global warming.**

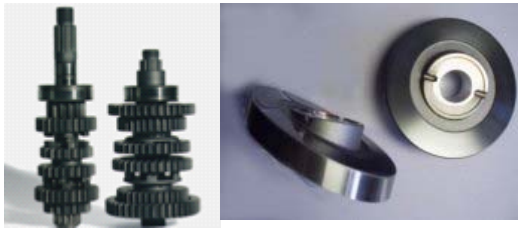




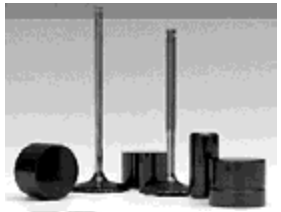
Intergovernmental Panel on Climate Change, 2001
http://www.ipcc.ch

DLC for Friction Control in Engines



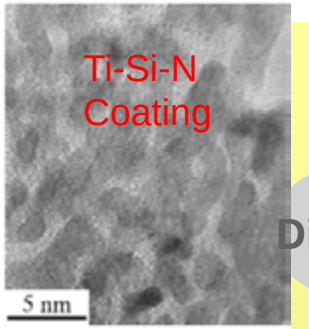


rpm-mag.com

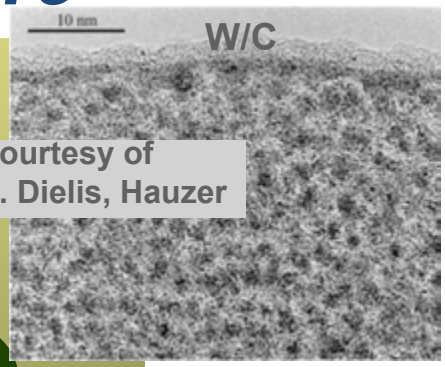


There are so many coatings out there

Unique Structure and Chemistry



W.J. Meng, et al. J. Mater. Res., Vol. 17, No. 10, Oct 2002



Courtesy of R. Dielis, Hauzer

Diamond

TiAlN

TiCN

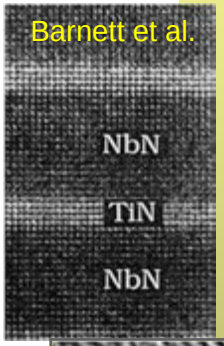
TiNALOX™

DLC

TiC

B_4C

TiN



MultiLayer

CBN

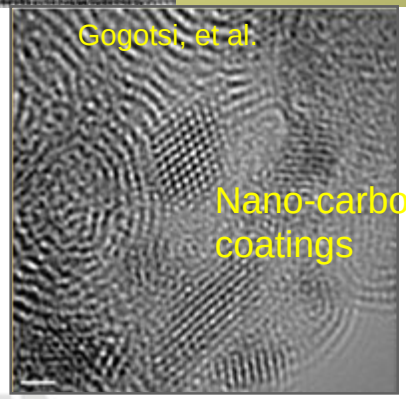
CrN

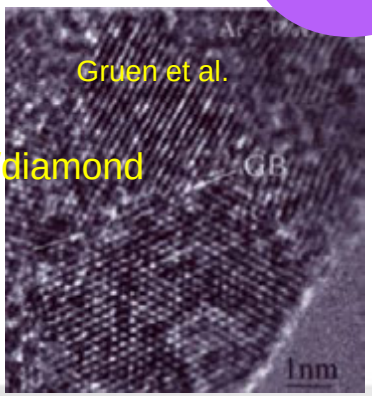
WC-C

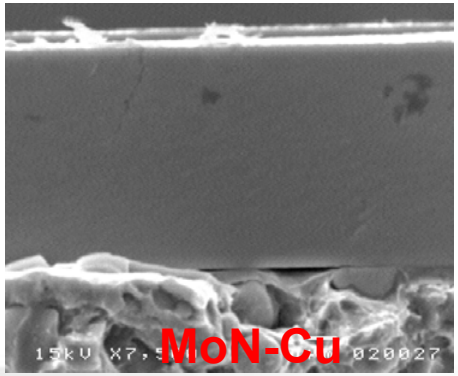
TiB_2

ALOX™

Courtesy of G. Lake



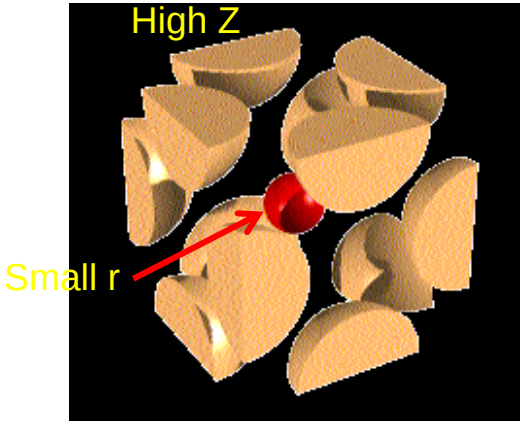




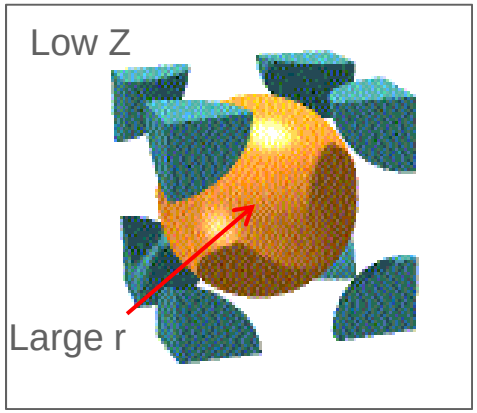
Courtesy of P. Hovsepian and D. Münz

Argonne's Approach to Design of Low-friction nc-Coatings

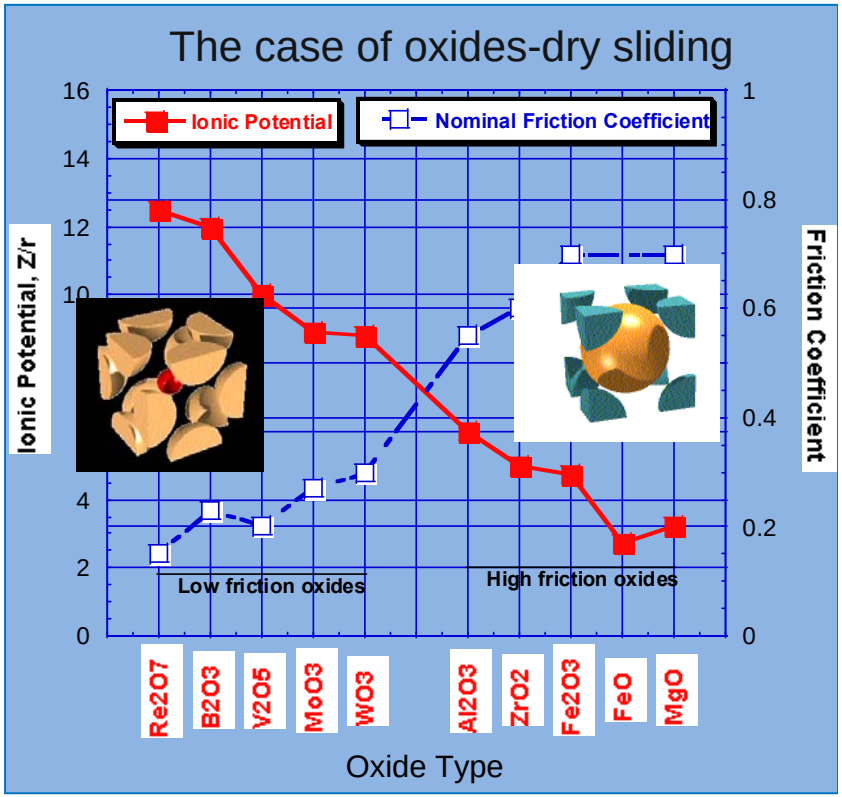
•**Ionic Potential; φ = Z/r** where;
Z is cationic charge and
r is the radius of the cation



High **φ**



Low **φ**

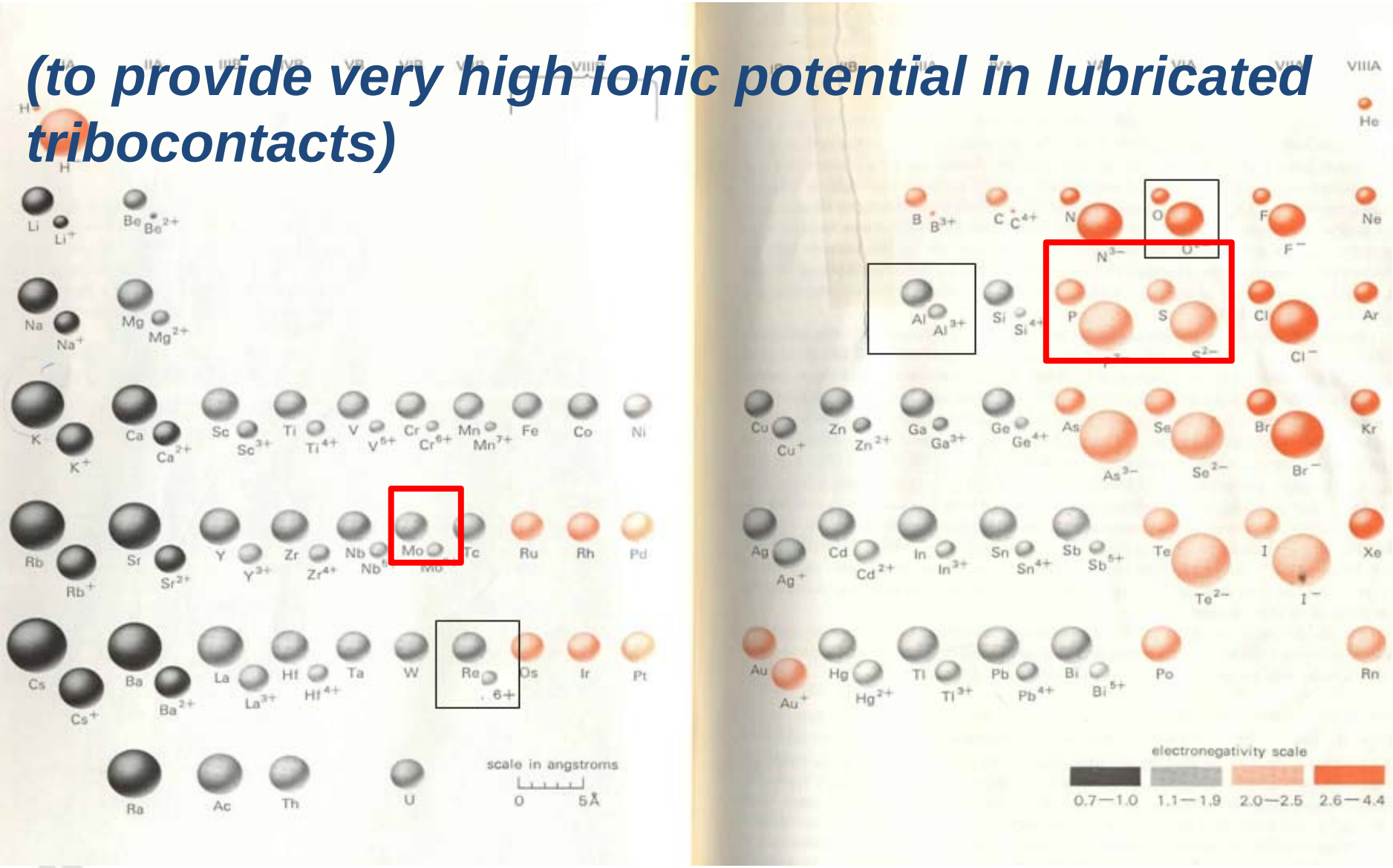


In general, higher the ionic potential, the greater the extent of screening by surrounding anions (such as oxygen, in the case of oxides (open air); sulfur, phosphorous, chlorine, etc. in the case of sulfides, phosphates, chlorides (lubricated contacts).

Erdemir, et al., Int. J. Mol. Sci., 6 (2005) 203

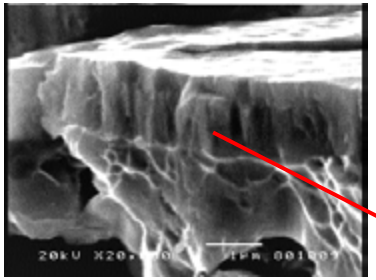
Selecting the Right Kinds of Elements

(to provide very high ionic potential in lubricated tribocontacts)

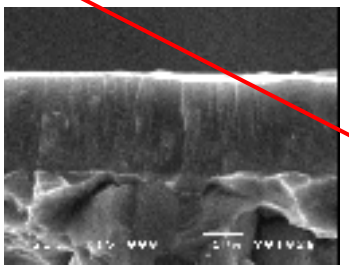


Development of Lubricant-Friendly MoN-Cu-based Nano- composite coatings

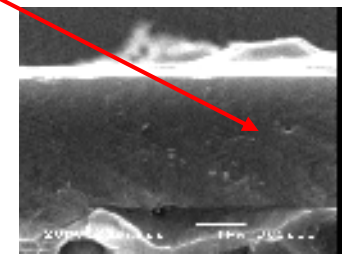
MoN Coating



0% Cu

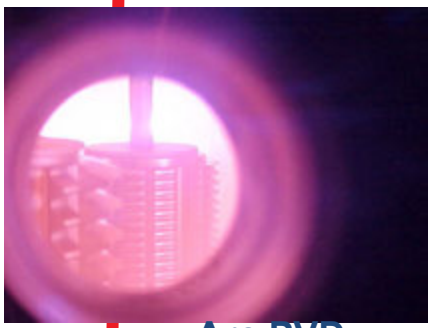


0.6% Cu

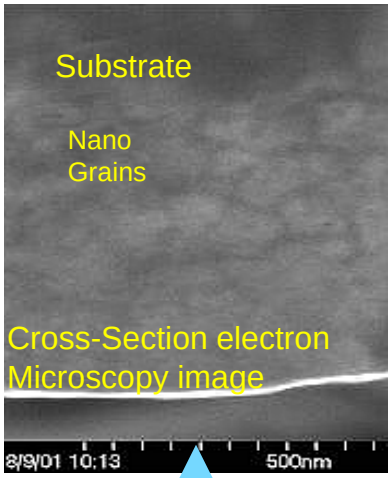


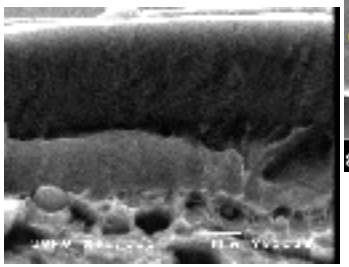
1.2%Cu

After ion etching

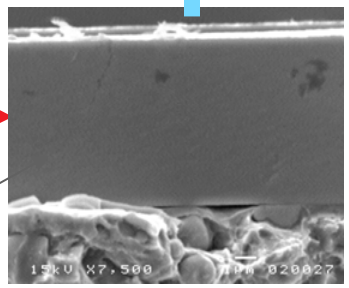


Arc PVD





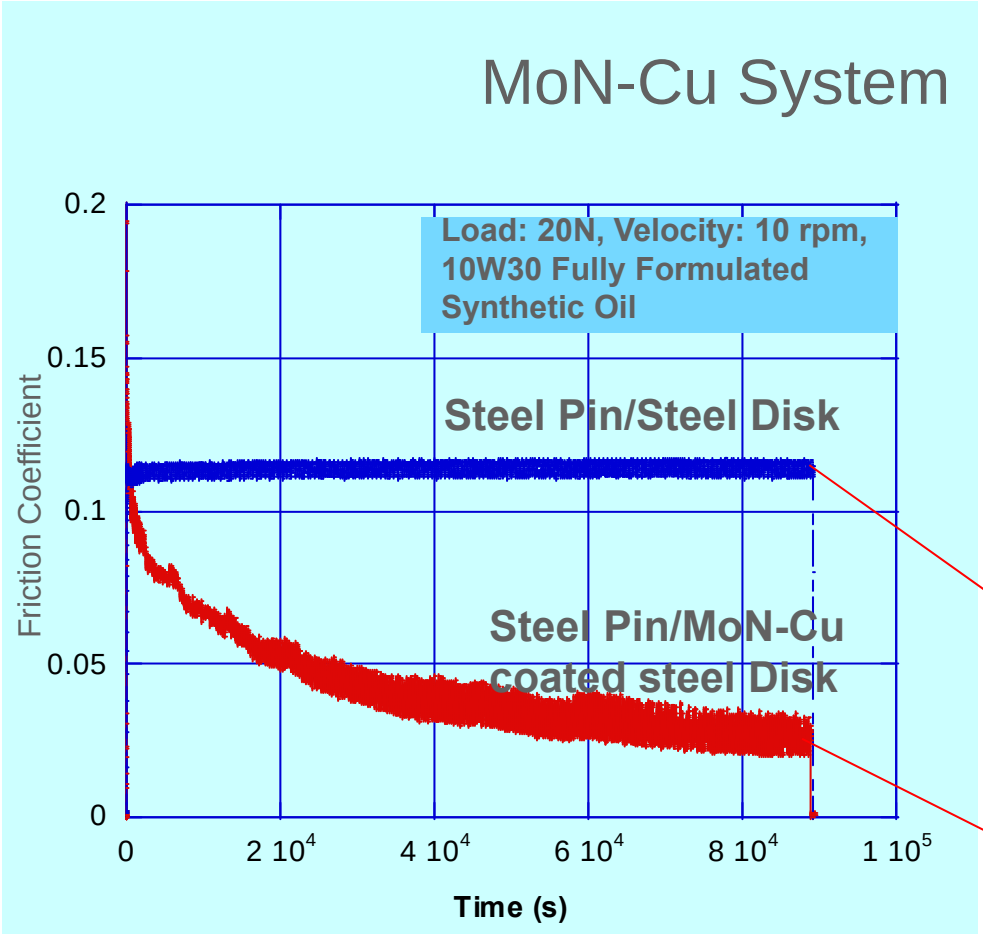
Transition from a columnar grain morphology to a featureless, fully-dense grain morphology

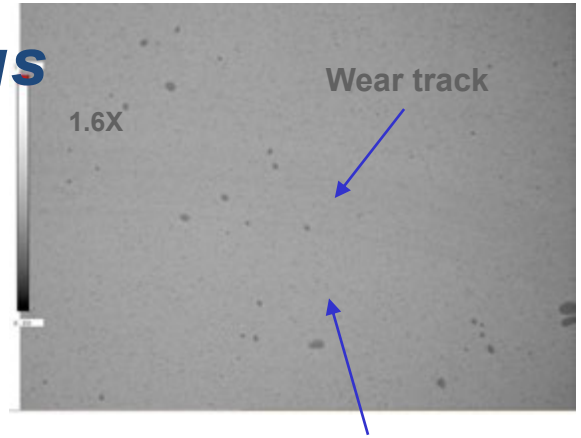


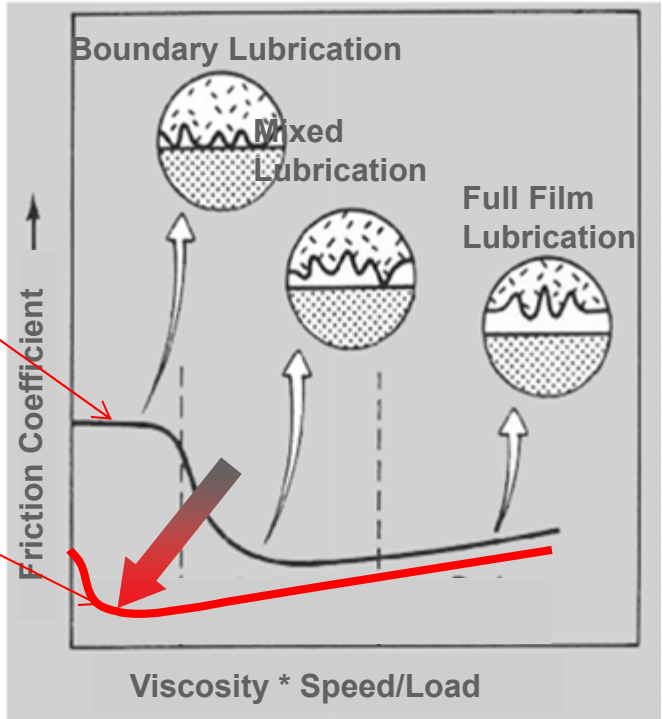
Hardness tunable between 30 to 60 GPa

2.2 % Cu (or more)

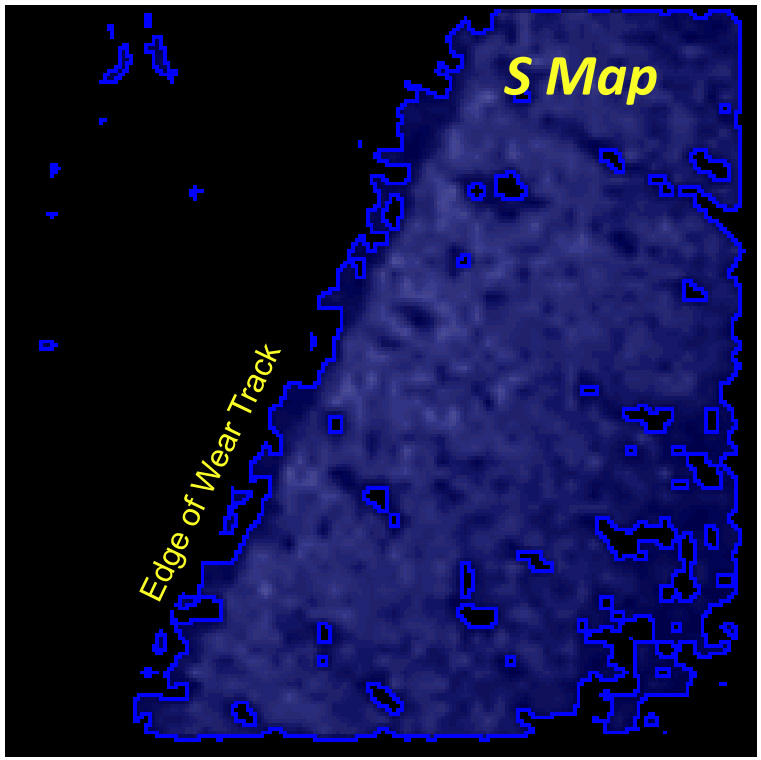
Superlow Friction and Wear Enabled by Such Designer Coatings

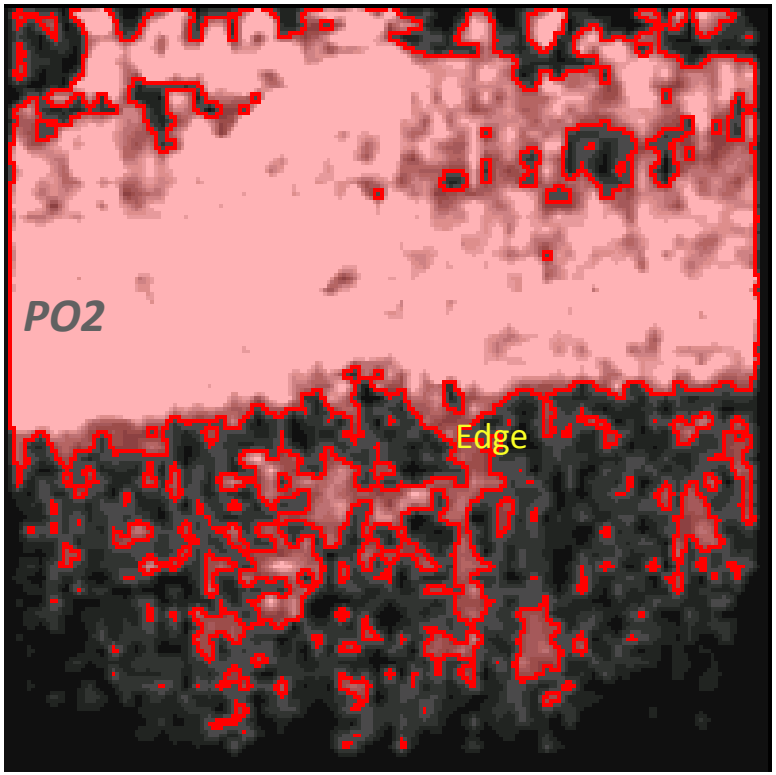






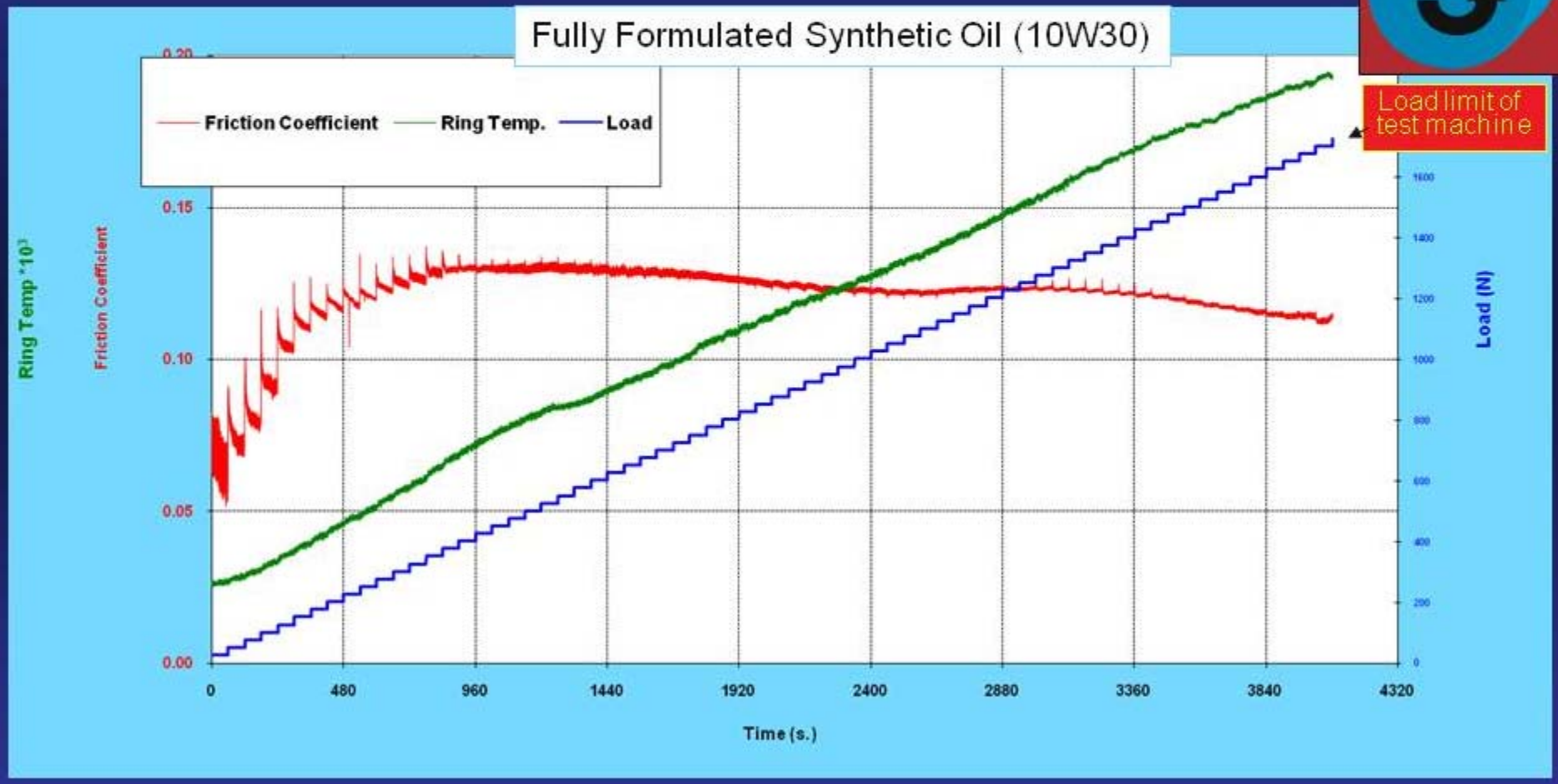
ToF-SIMS Images of Wear Tracks of MoN-Cu nc-coating



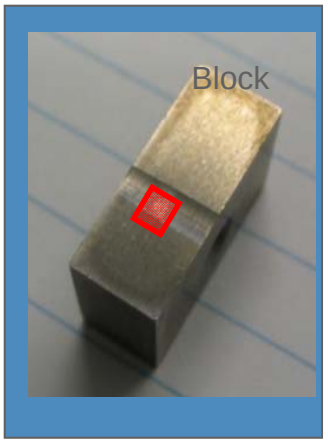


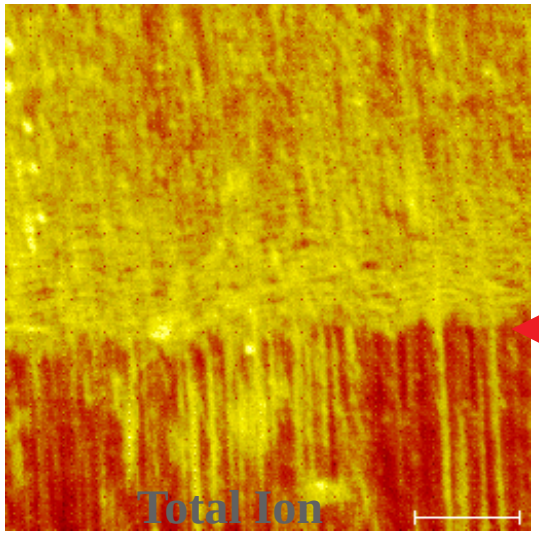
Extreme Resistance of Such Coatings to Scuffing

Nanocomposite MoN-Cu-coated Steel

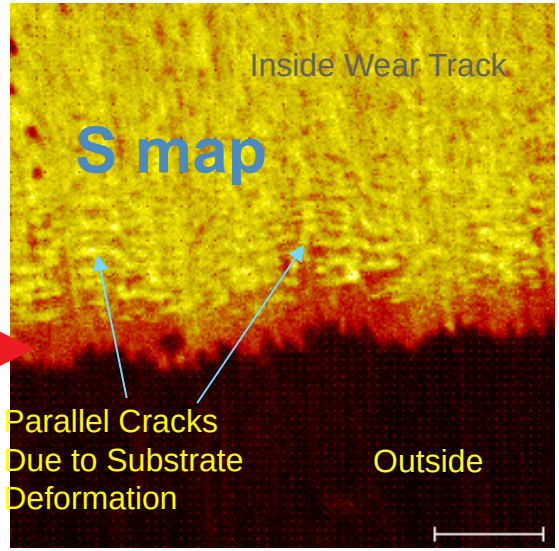


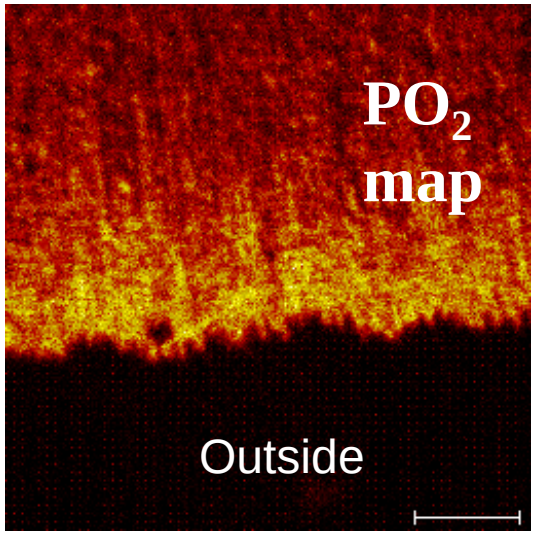
Superior Ability to Form Low-shear, Highly-protective Tribofilms





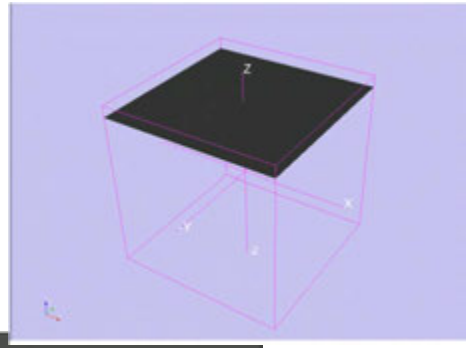
Border Between Inside and Outside of Wear Track

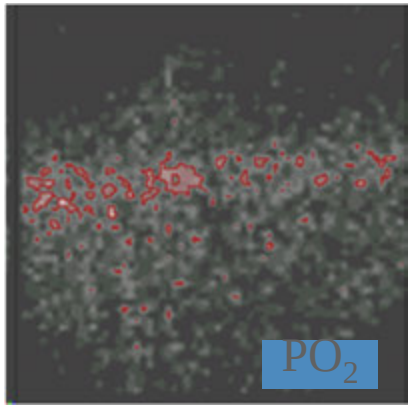


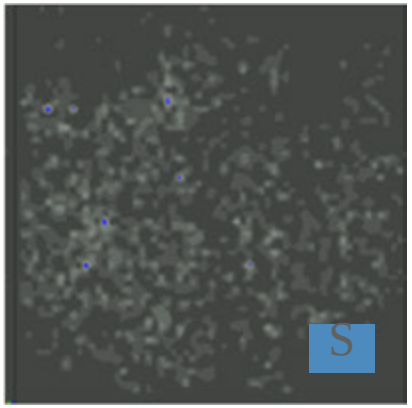


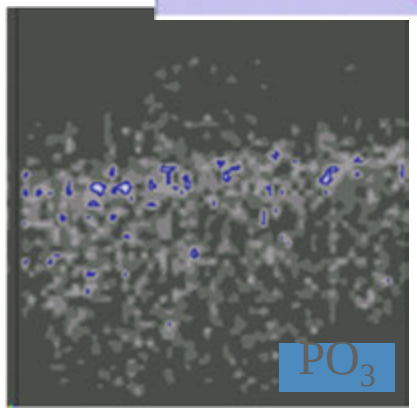
These findings suggest very strong chemical interactions between coating and lubricant additives

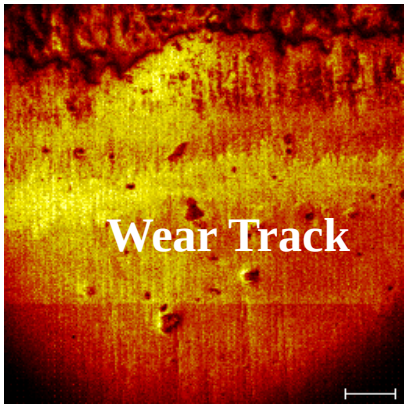
MoN-Cu–Scuffing test Slices



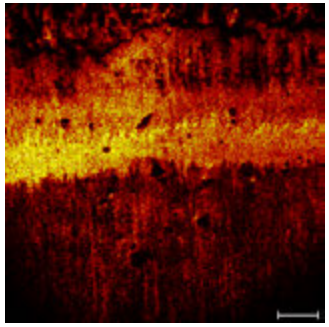




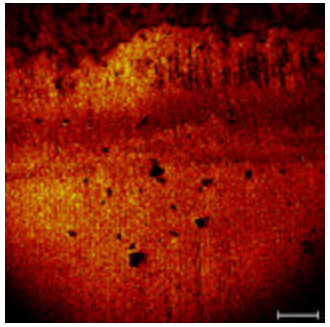




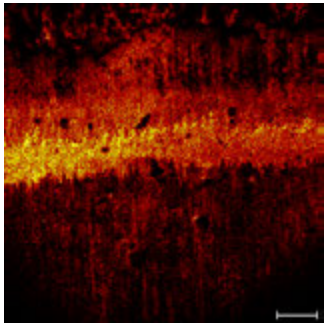
Total Ion



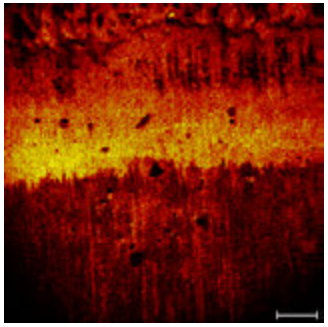
PO_2



S



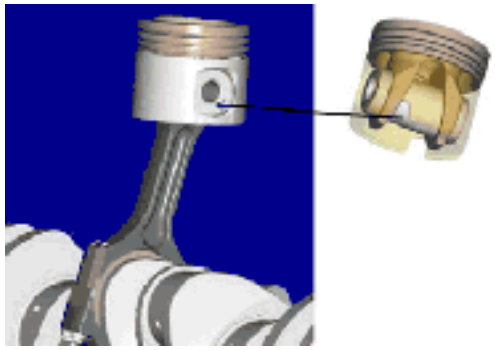
PO_3



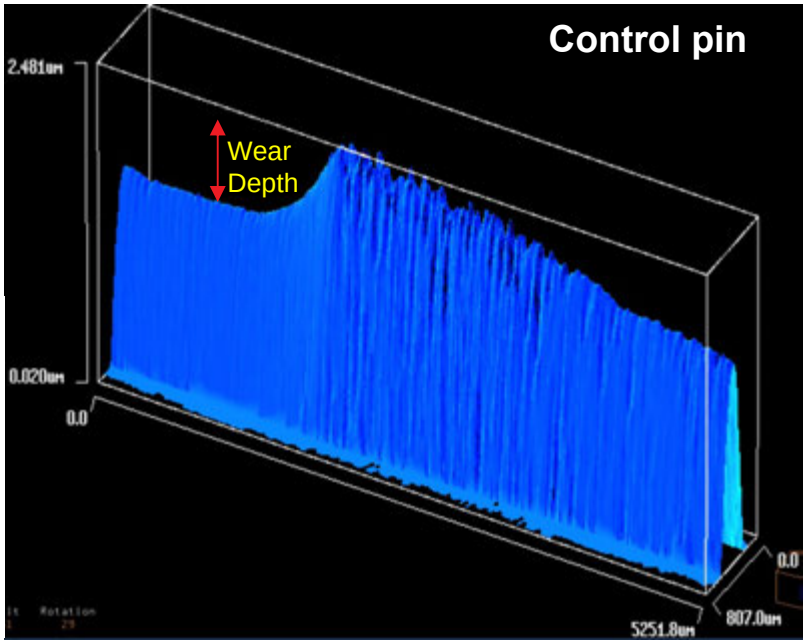
O

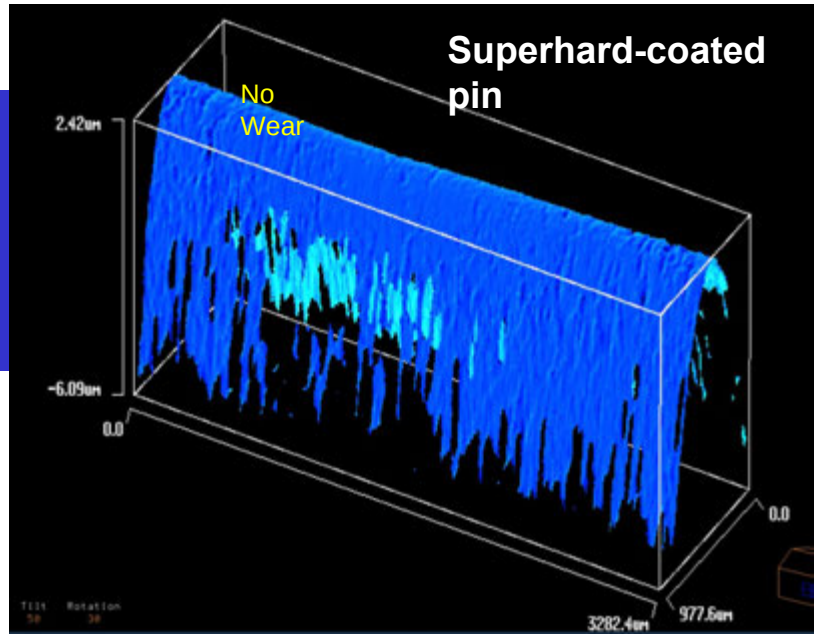
Fired Engine Tests:

Superhard Coatings on Piston Pins



Tests were run at high speed (hence high temperature) for 100 hours in a V8 engine.



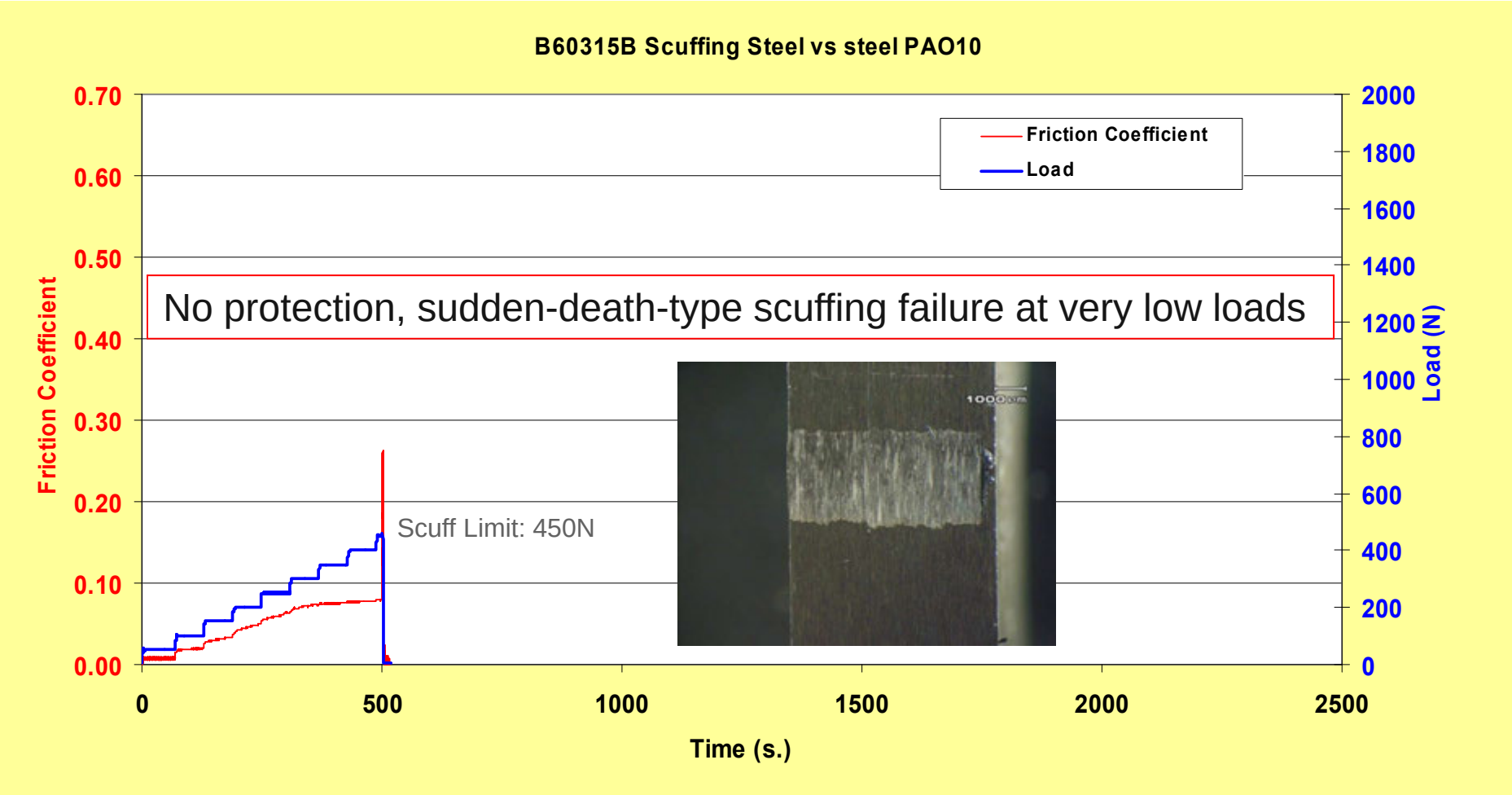


We had four coated pins in one bank of a V8 engine. The other 4 cylinders only had manganese phosphate coated pins (control pins).

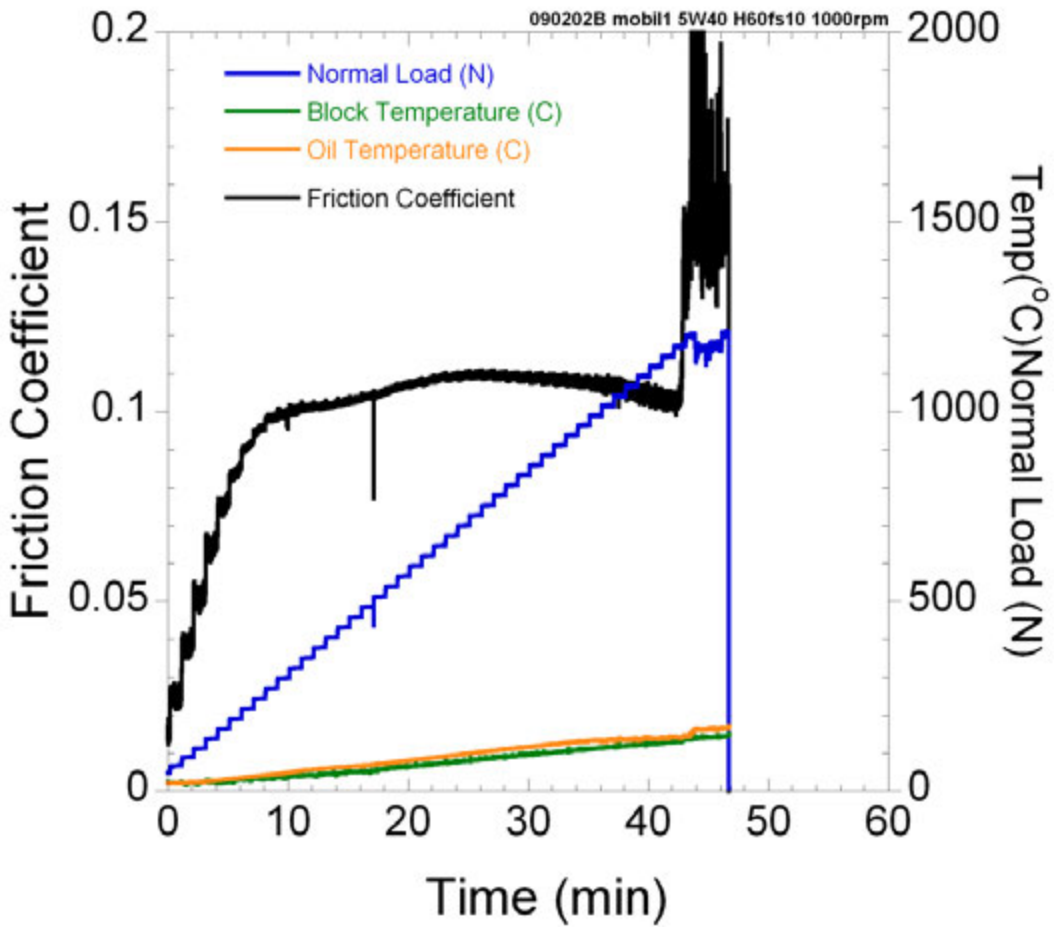
Designing Catalytically Active nc-Coatings Producing In-situ DLC Films

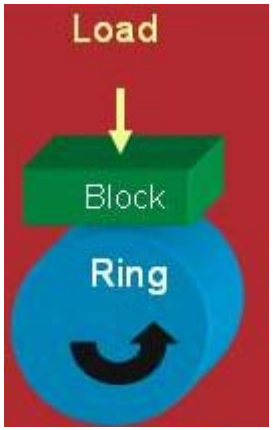
A Paradigm Shift in Lubricant/Materials Technologies

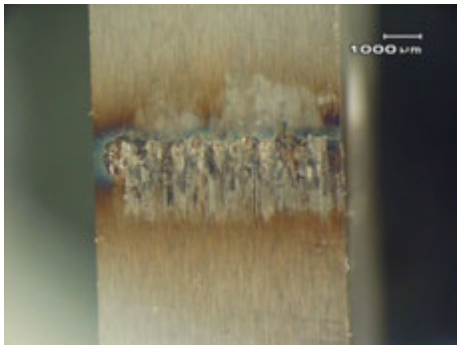
Scuff Resistance of Bare Steel in Base Oils Block on Ring Tests



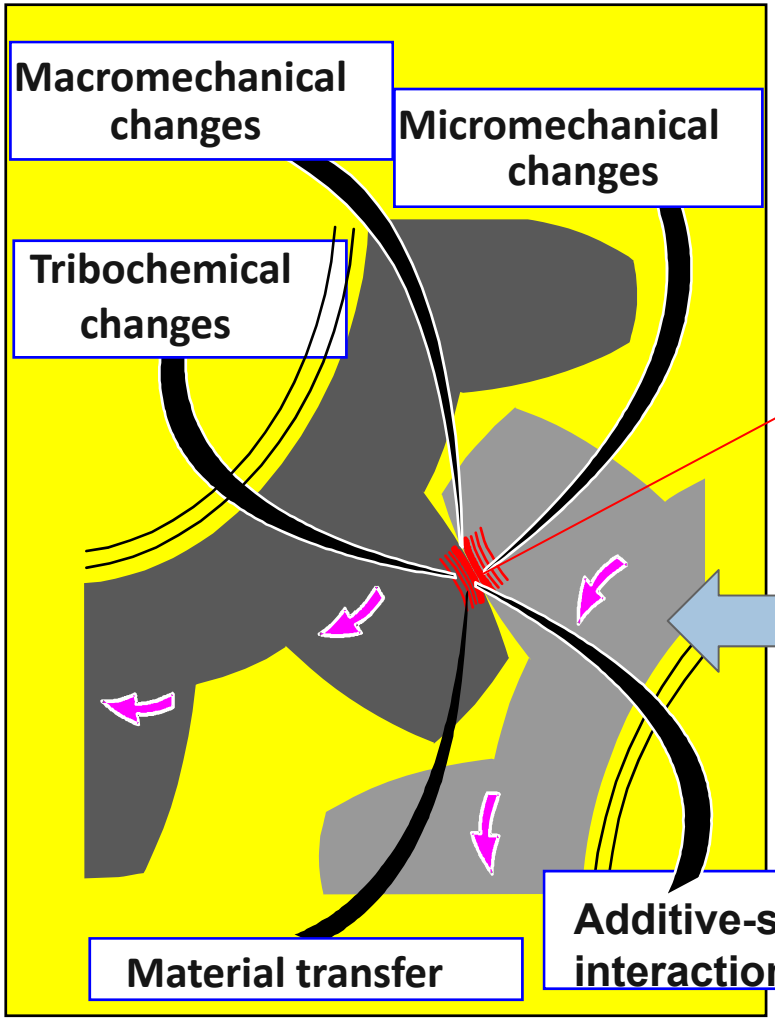
Scuffing Resistance of Steel/Steel in Fully Formulated Synthetic Oil



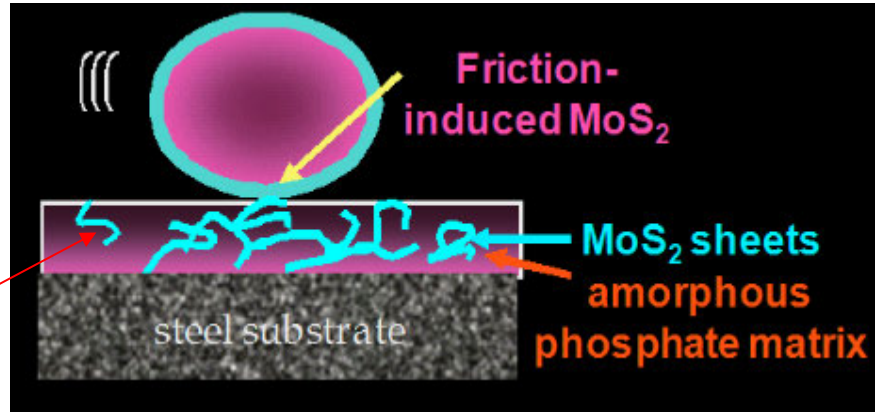


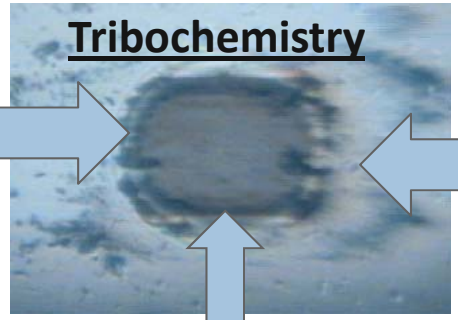


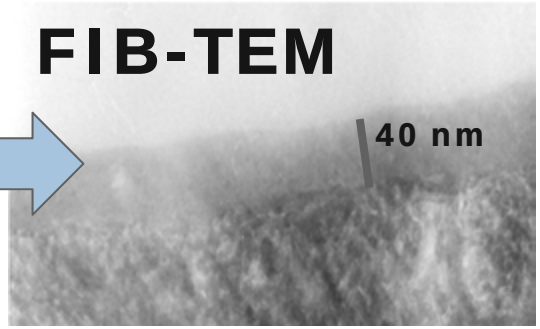
Fundamentals of Lubricated Contacts

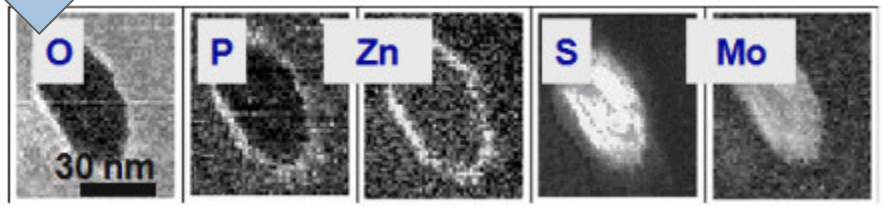


Courtesy of K. Holmberg, VTT/Finland









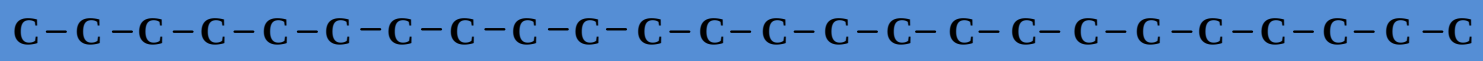
Courtesy of Prof. J. –M. Martin

Big Question to Answer:

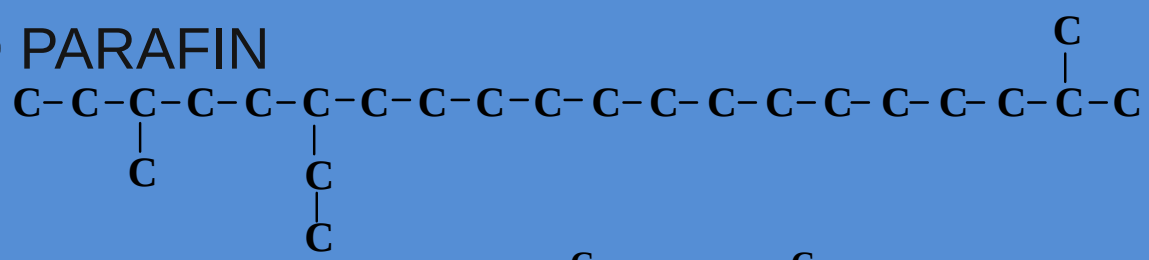
Can we extract boundary films directly from base hydrocarbon oils that are as good as the ones that result from fully formulated oils?

Typical Base Oil Structures

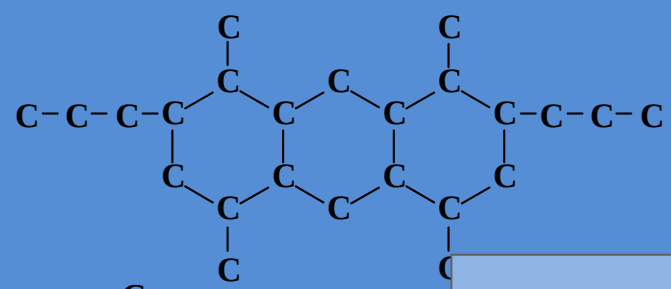
- NORMAL PARAFFIN



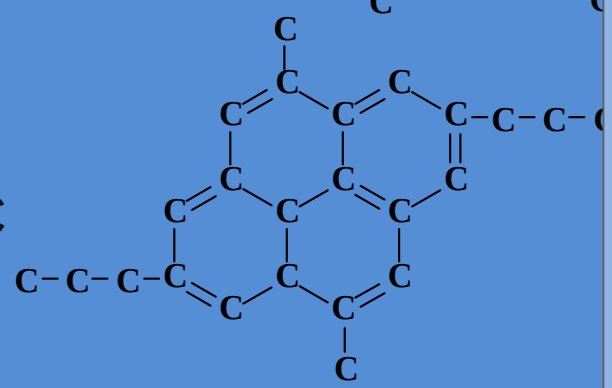
- ISO PARAFIN



- NAPHTHENIC



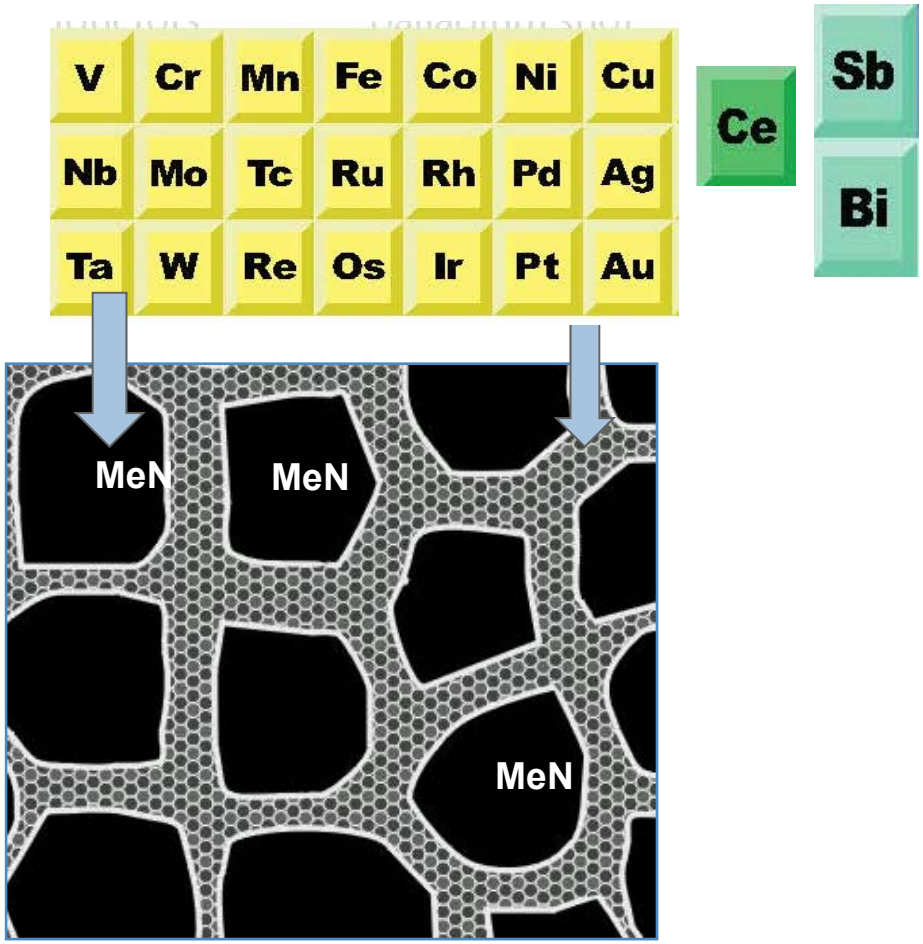
- AROMATIC



Bottom-Line: They are all hydrocarbons (made of carbon and hydrogen).

Approach: Can we tear them apart and deposit bits and pieces on sliding surfaces as carbon-based boundary films?

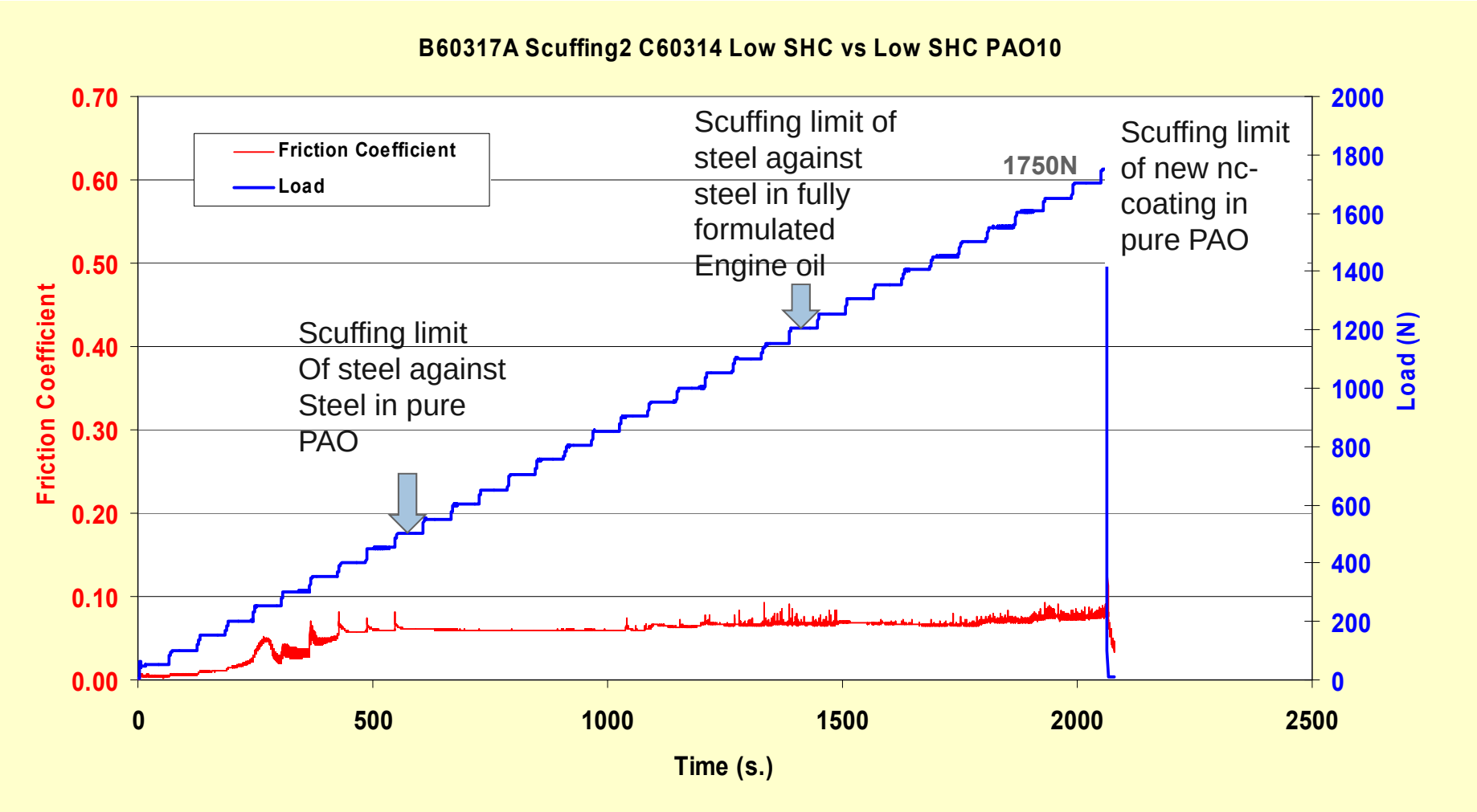
Design of nanocomposite coatings that can extract DLC-like boundary films from base (unformulated) oil molecules

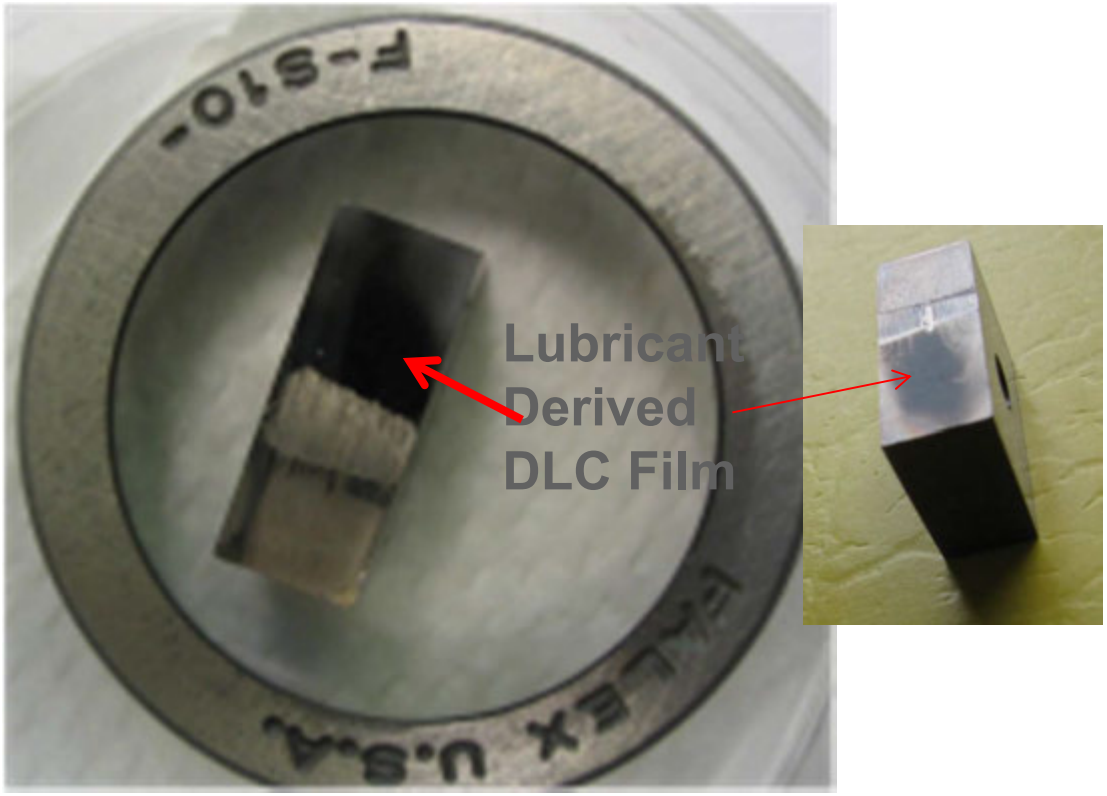


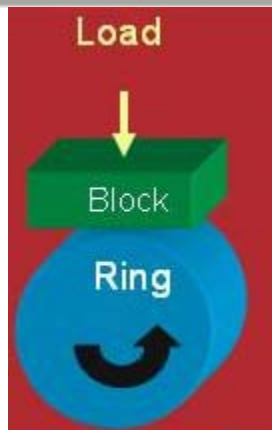
Patent Pending

Using this approach, we synthesized a number of nanocomposite coatings and demonstrated their carbon-rich boundary film forming abilities in base (unformulated) oils.

Block on Ring Tests

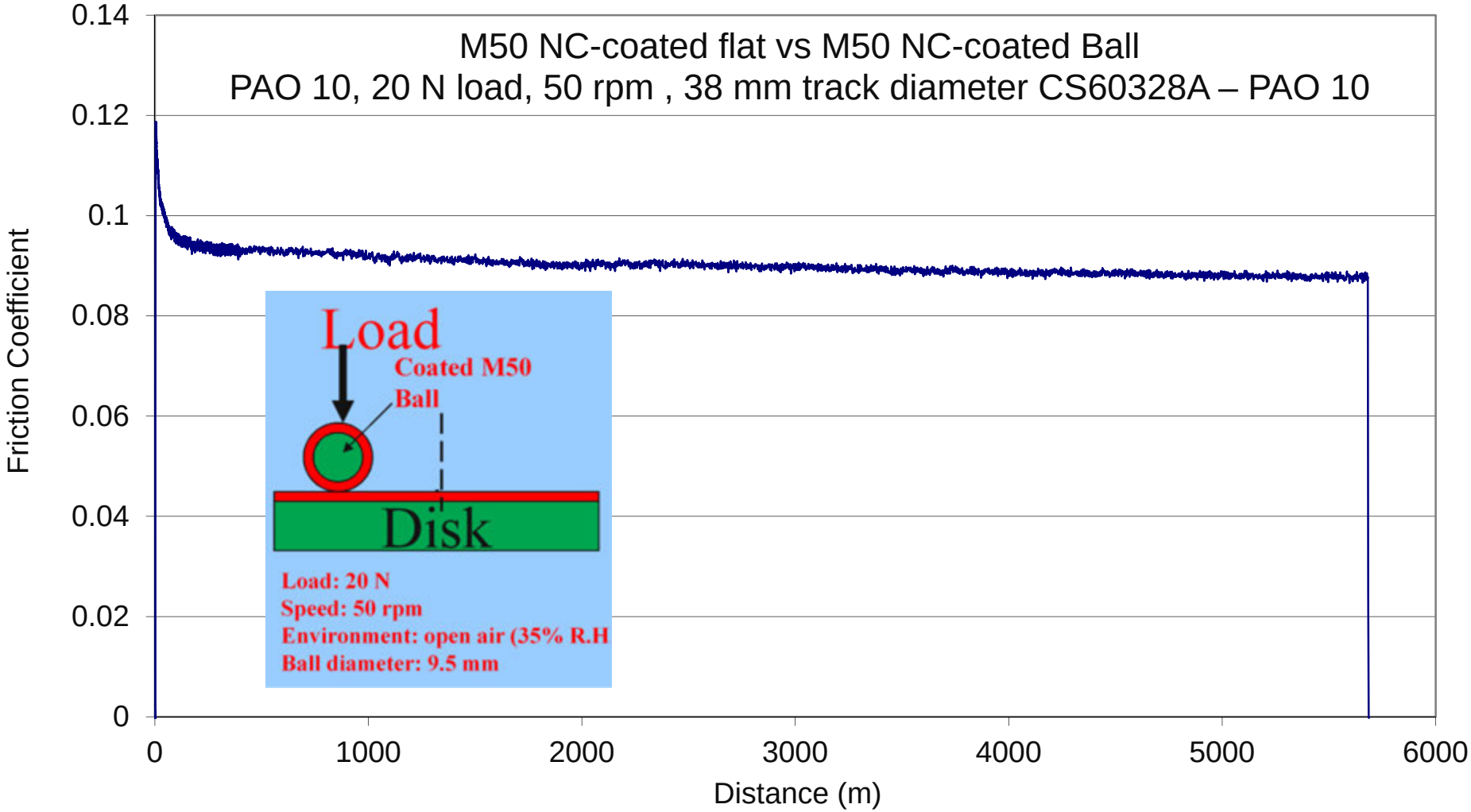




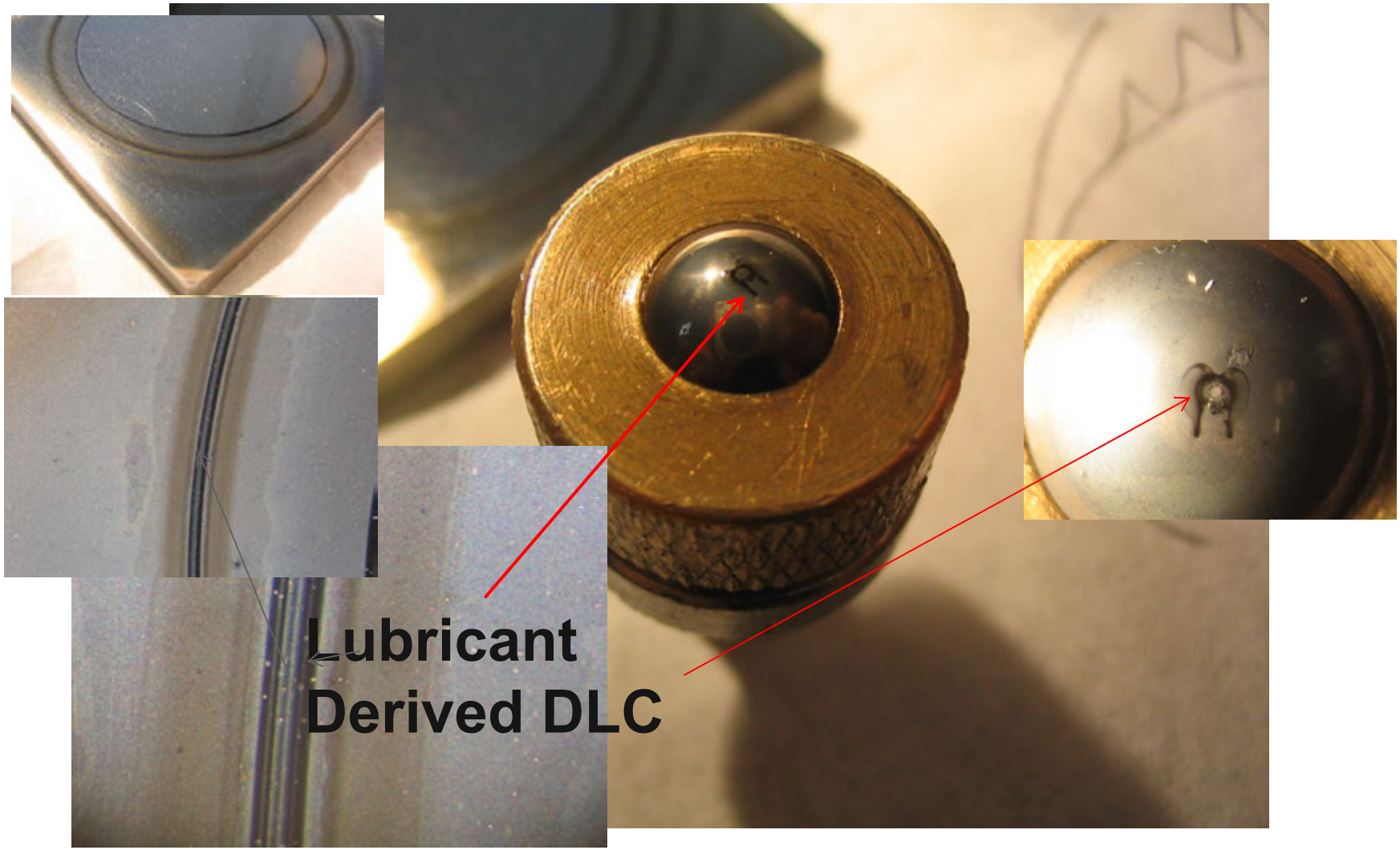


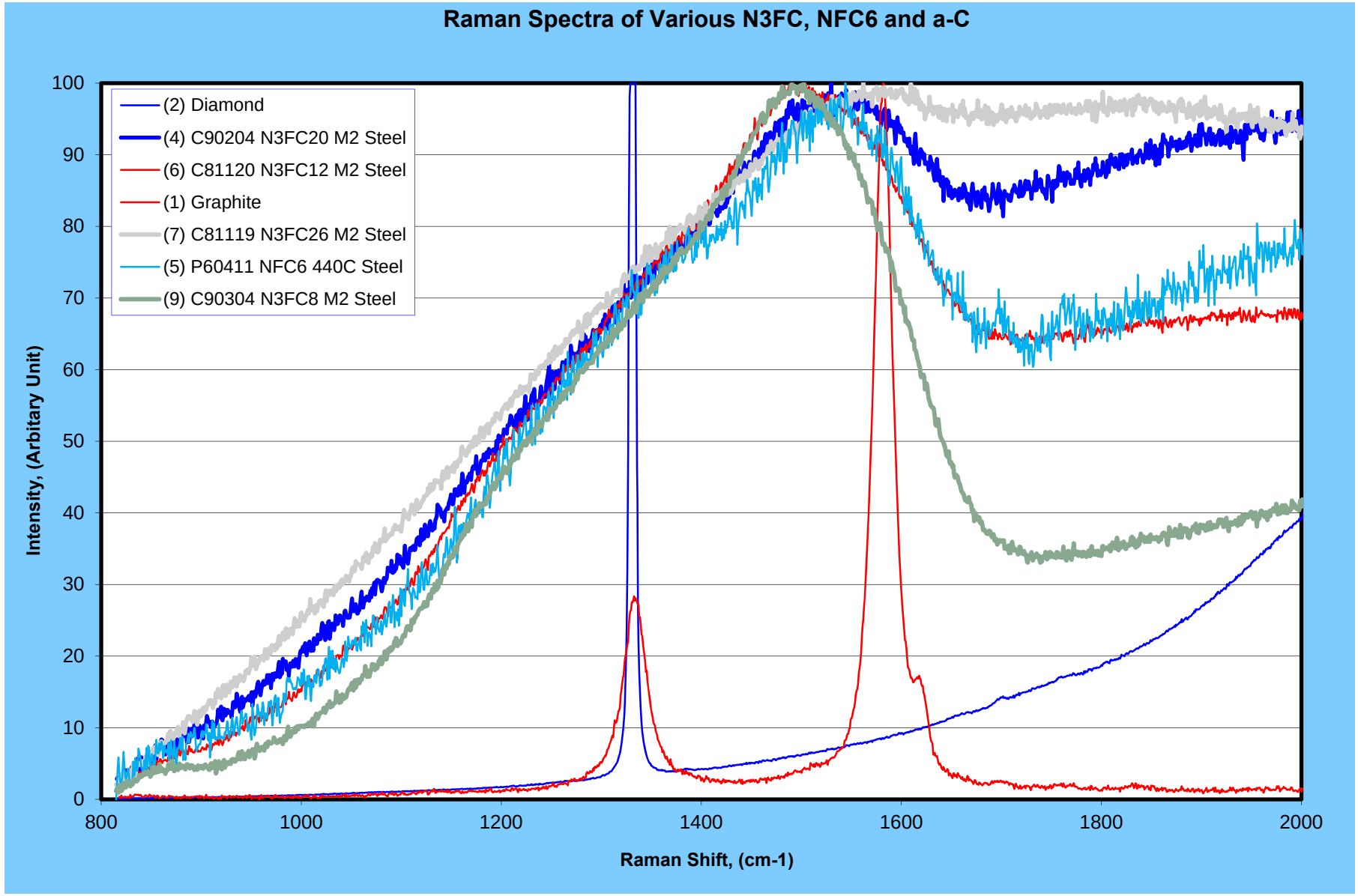
These designer coatings are able to extract or drive low-shear carbon films out of the base oils. Catalytic effect/activity (triggered by Re, Pd, Pt, etc.) appears to be the key mechanism.

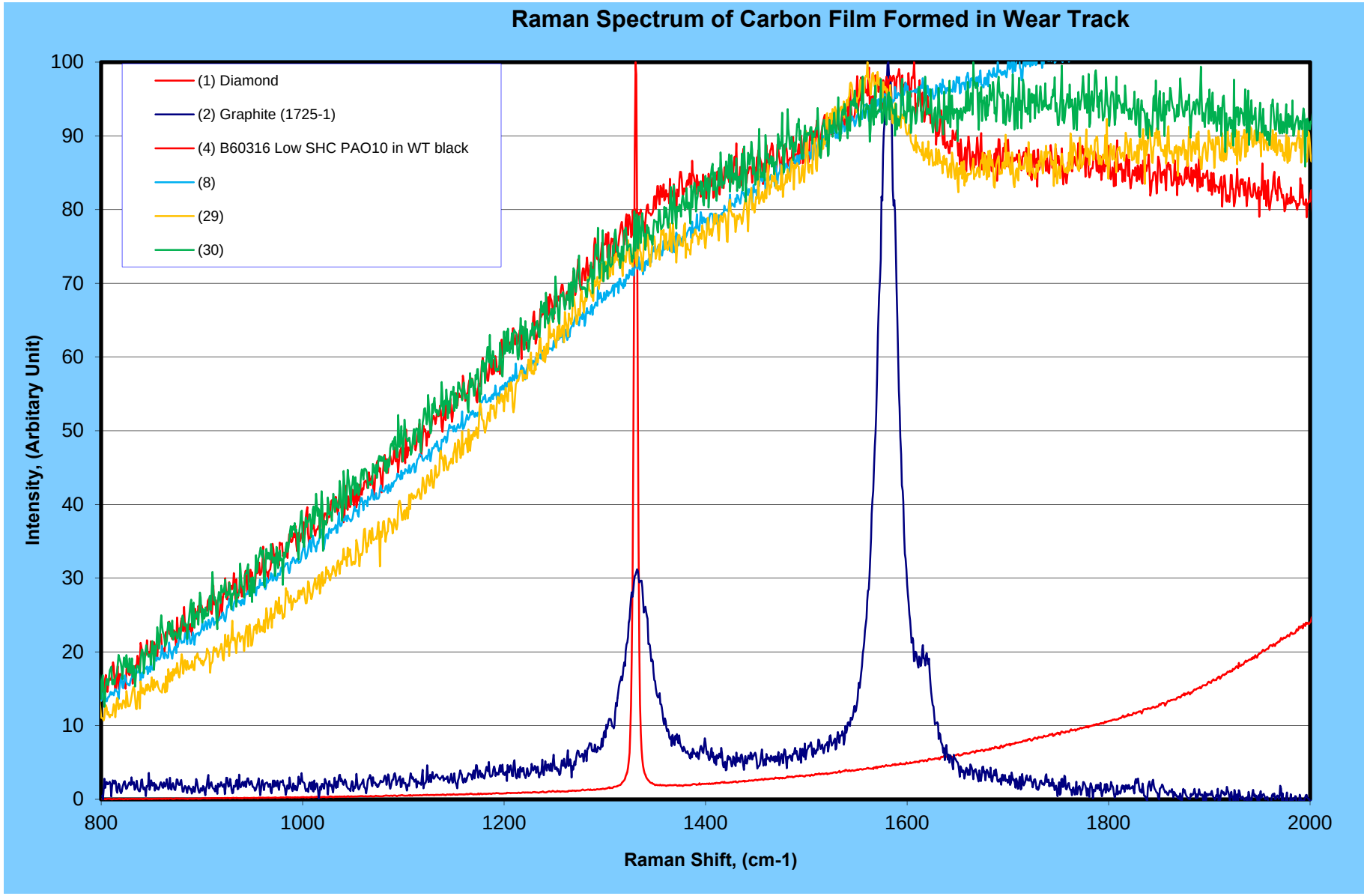
Pin-on-Disk Tribological tests with NC-Coated Ball Against NC-Coated Disk in PAO 10



Condition of Wear Track and Scar After Test




Raman Spectra of Various N3FC, NFC6 and a-C
(2) Diamond
(4) C90204 N3FC20 M2 Steel
(6) C81120 N3FC12 M2 Steel
(1) Graphite
(7) C81119 N3FC26 M2 Steel
(5) P60411 NFC6 440C Steel
(9) C90304 N3FC8 M2 Steel
Intensity, (Arbitary Unit)
0
10
20
30
40
50
60
70
80
90
100
800
1000
1200
1400
1600
1800
2000
Raman Shift, (cm-1)


Raman Spectrum of Carbon Film Formed in Wear Track
(1) Diamond
(2) Graphite (1725-1)
(4) B60316 Low SHC PAO10 in WT black
(8)
(29)
(30)
Intensity, (Arbitary Unit)
Raman Shift, (cm-1)
0
10
20
30
40
50
60
70
80
90
100
800
1000
1200
1400
1600
1800
2000

Summary:

- Novel nc-coatings described here may offer high potential to reduce friction and to increase resistance to wear, and scuffing in engine and drivetrain components.
  - Use of catalytically active ingredients in a hard nitride coating seems to derive DLC-like boundary films from the base oil and thus enable very high resistance to wear and scuffing.
- When scaled-up and implemented, such coatings may significantly increase efficiency and durability in future engines.