Molybdenum Additive Technology for Engine Oil Applications

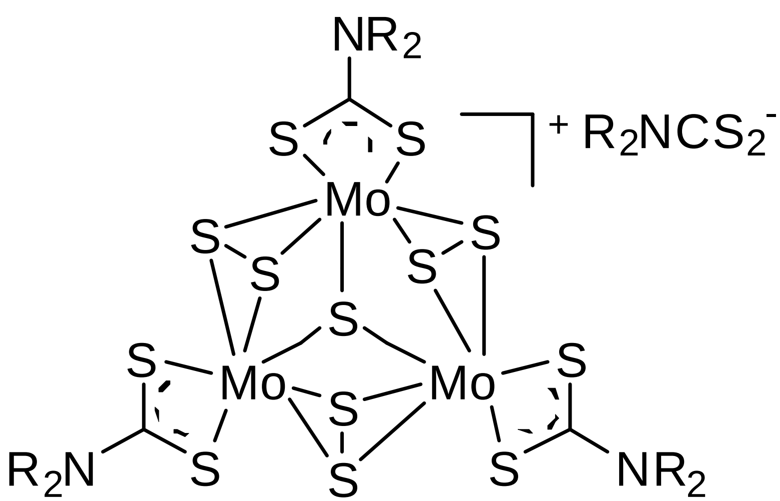
Presented at the Japan Tribology on the 6th-11th September 2009 in Kyoto, Japan

Ben Elvidge and Jai Bansal

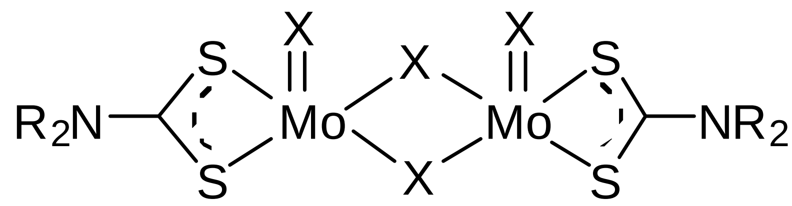
Outline

- Introduction to molybdenum oil additives
- Part 1: Molybdenum trimer at Conventional Material Contacts
  - HFRR (friction)
  - Seq. IVA
- Part 2: Molybdenum trimer at Non-Conventional Material Contacts
  - Steel-DLC
  - Steel-AluSil

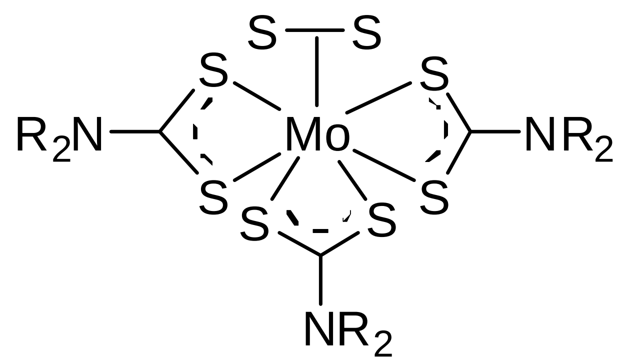
Introduction to molybdenum oil additives



Trinuclear



Dinuclear (X = O / S)



R = hydrocarbyl

Mononuclear

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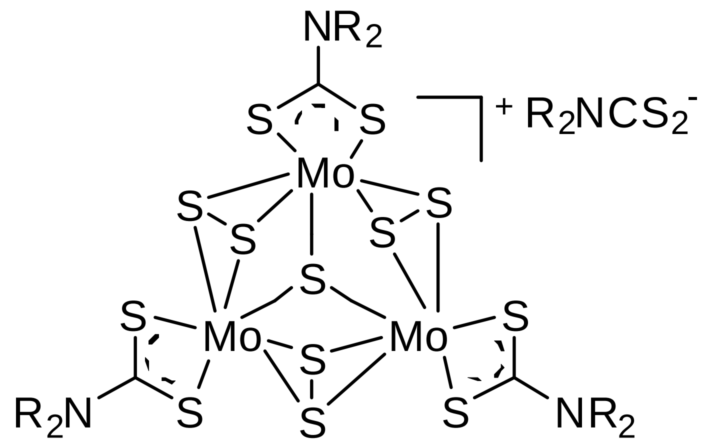
Introduction to Molybdenum Trimer

- Trinuclear molybdenum-sulfur DTC cluster
- More sulfur in the core facilitating MoS_2 production
- Molybdenum is in +(IV) oxidation state as in MoS_2
- Core sulfur is powerful peroxide decomposing antioxidant
- Layered structure resembles MoS_2



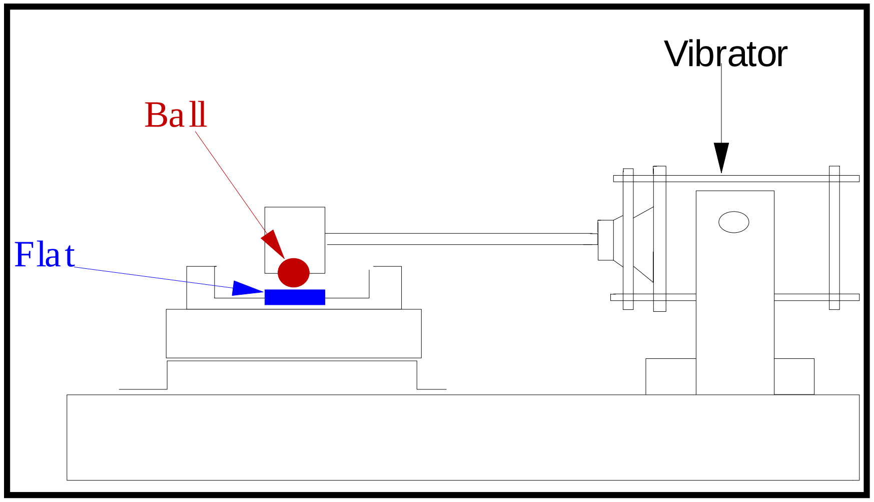
Trinuclear

R = hydrocarbyl

Part 1: Molybdenum Trimer at Conventional Material Contacts

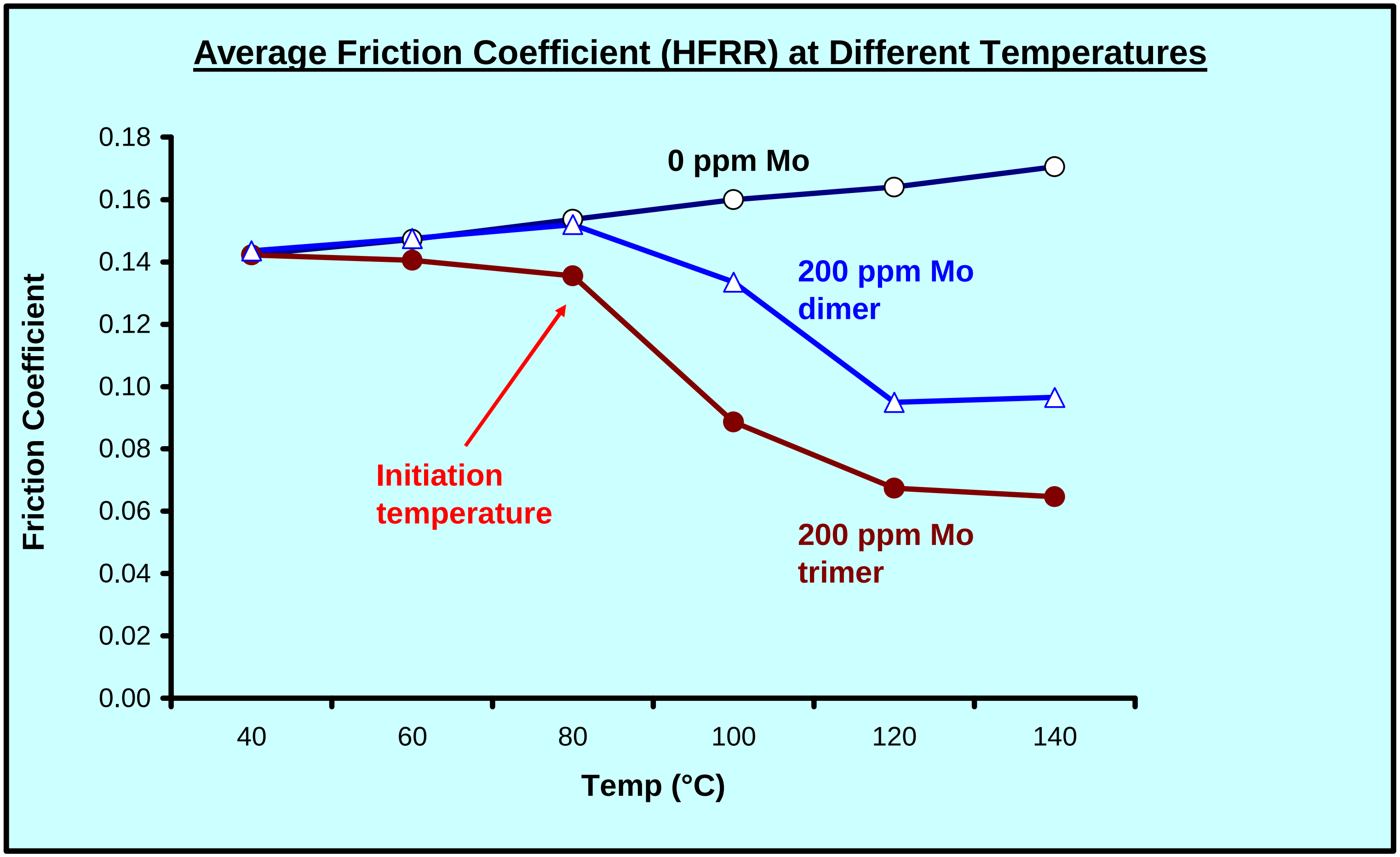
Introduction to HFRR Methodology

- Boundary friction measured as a function of time
- 6 mm diameter stainless steel ball stainless steel plate
- Reciprocating motion
- Stroke Length: 20 µm - 2.0 mm
- Temp. range of 40 °C to 140 °C
- Frequency: 10 - 50 Hz
- Load: 1 - 10 N



Steel on Steel: HFRR (1)

Mo trimer produces much lower friction coefficient than Mo dimer



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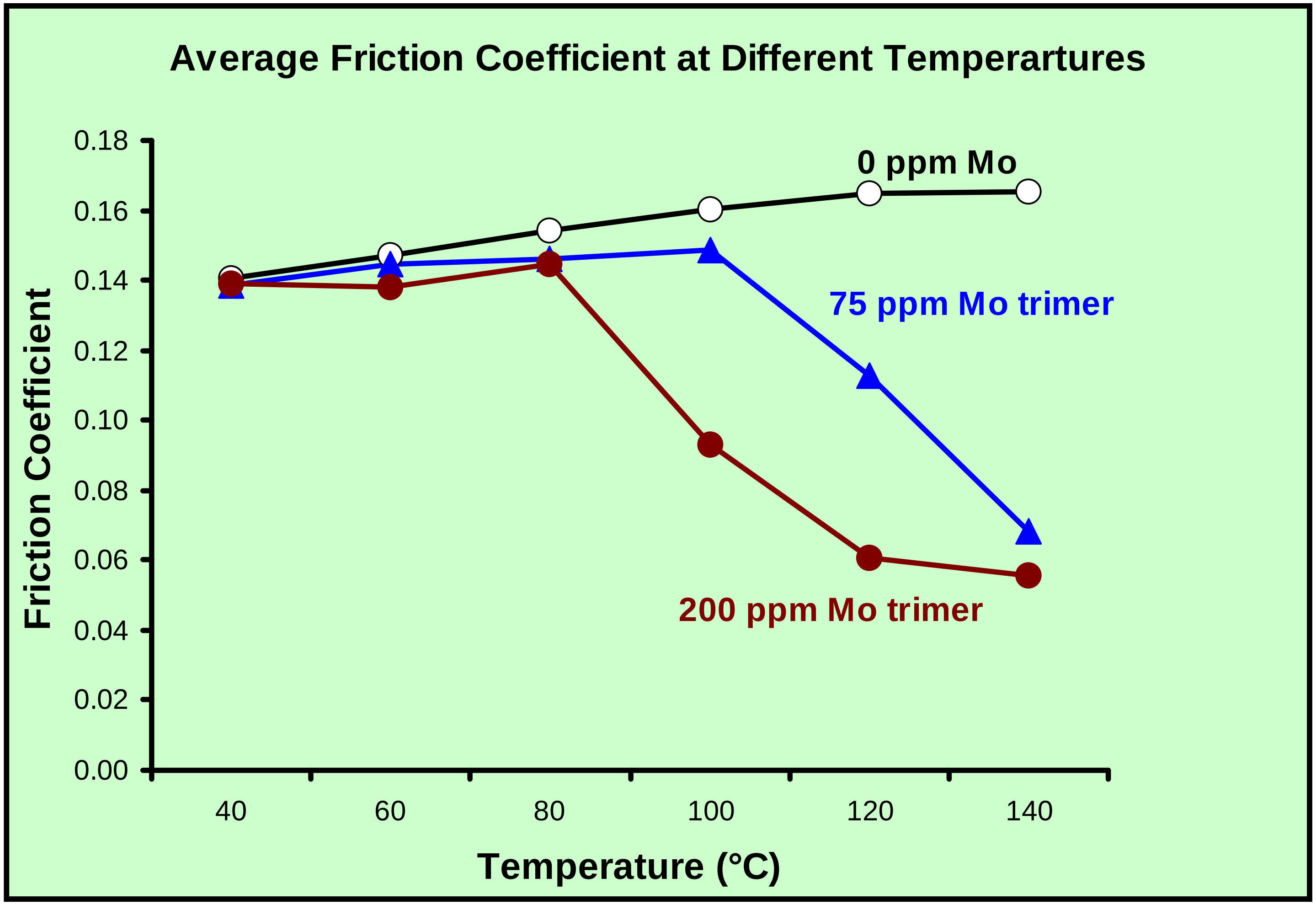
Steel on Steel: HFRR (2)

- At much reduced molybdenum treat-rate, low final friction coefficients in the HFRR can still be achieved
- At end-point (140 °C) on step-ramp profile, final friction coefficient for 75 ppm Mo formulation similar to that obtained at higher treat-rates (200 ppm)

[Mo] (ppm)	Final Friction Coefficient
0	0.16
75	0.07
200	0.06

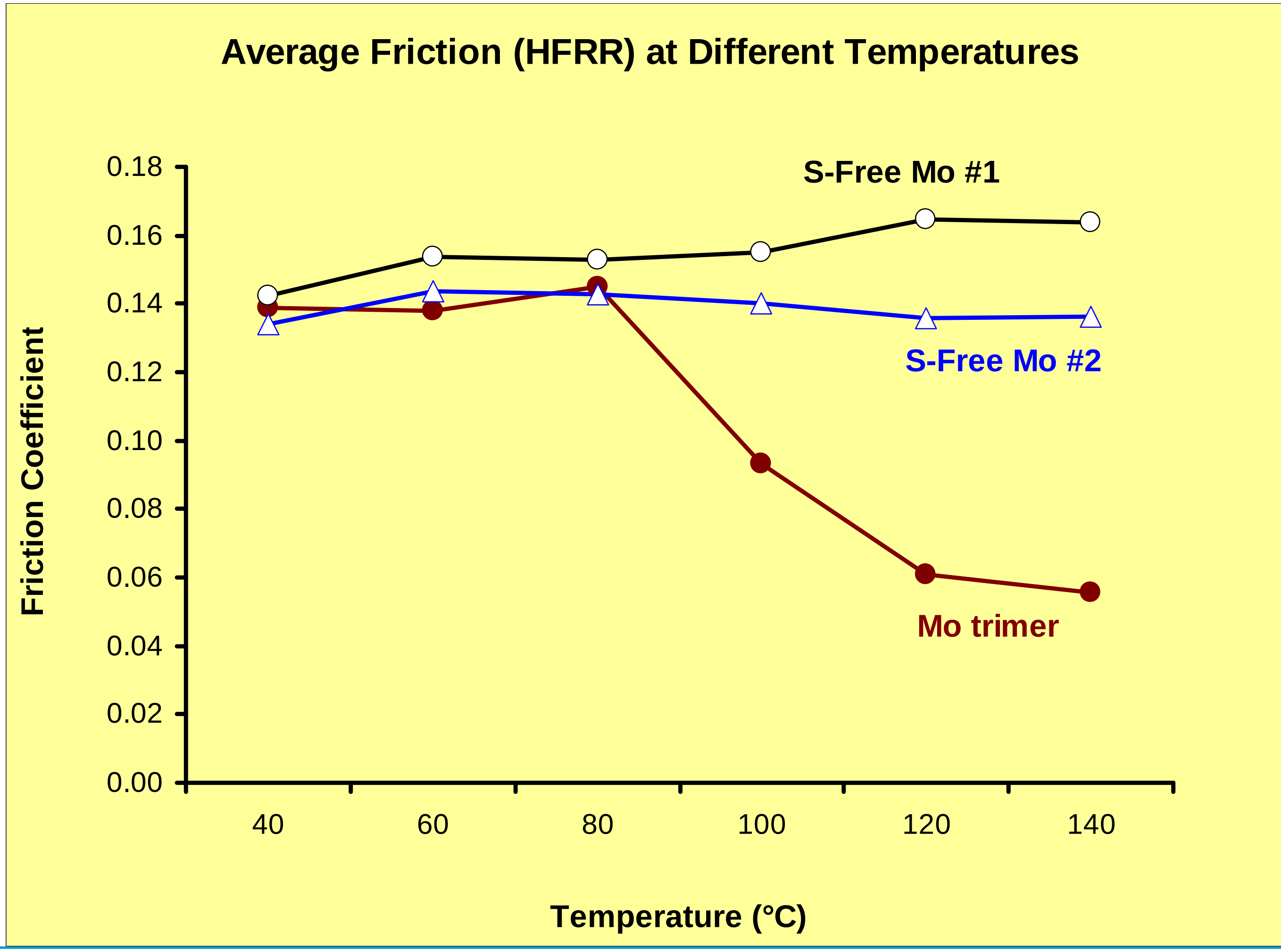
Steel on Steel: HFRR (3)

Despite a very similar final friction coefficient, lower Mo concentration result in slower rate of activation



Steel on Steel: HFRR (4)

Sulphur-free molybdenum species show much higher friction coefficients



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Engine Test Data: Introduction to Seq. IVA (1)

- Seq. IVA procedure (ASTM D 6891)
- "Low temperature" wear test
- Camshaft lobe wear (overhead camshaft engine) key parameter
- 1994 Nissan KA24E, 2.4-liter, water-cooled, fuel-injected engine, 4-cylinder in-line, overhead camshaft with 2 intake valves and 1 exhaust valve per cylinder
- The test is a 100-hour test involving 100 hourly cycles
  - Each cycle consists of 2 operating modes (stages)
  - Unleaded "Haltermann KA24E Green" fuel used
- 12 cam lobes measured at 7 locations at end of test
  - Surface profilometer used to measure maximum depth of wear
  - Measurements of wear on all 7 positions of each lobe are added together
  - All 12 lobe measurements are averaged for the wear result
- Molybdenum trimer is extremely effective in controlling wear in Seq. IVA

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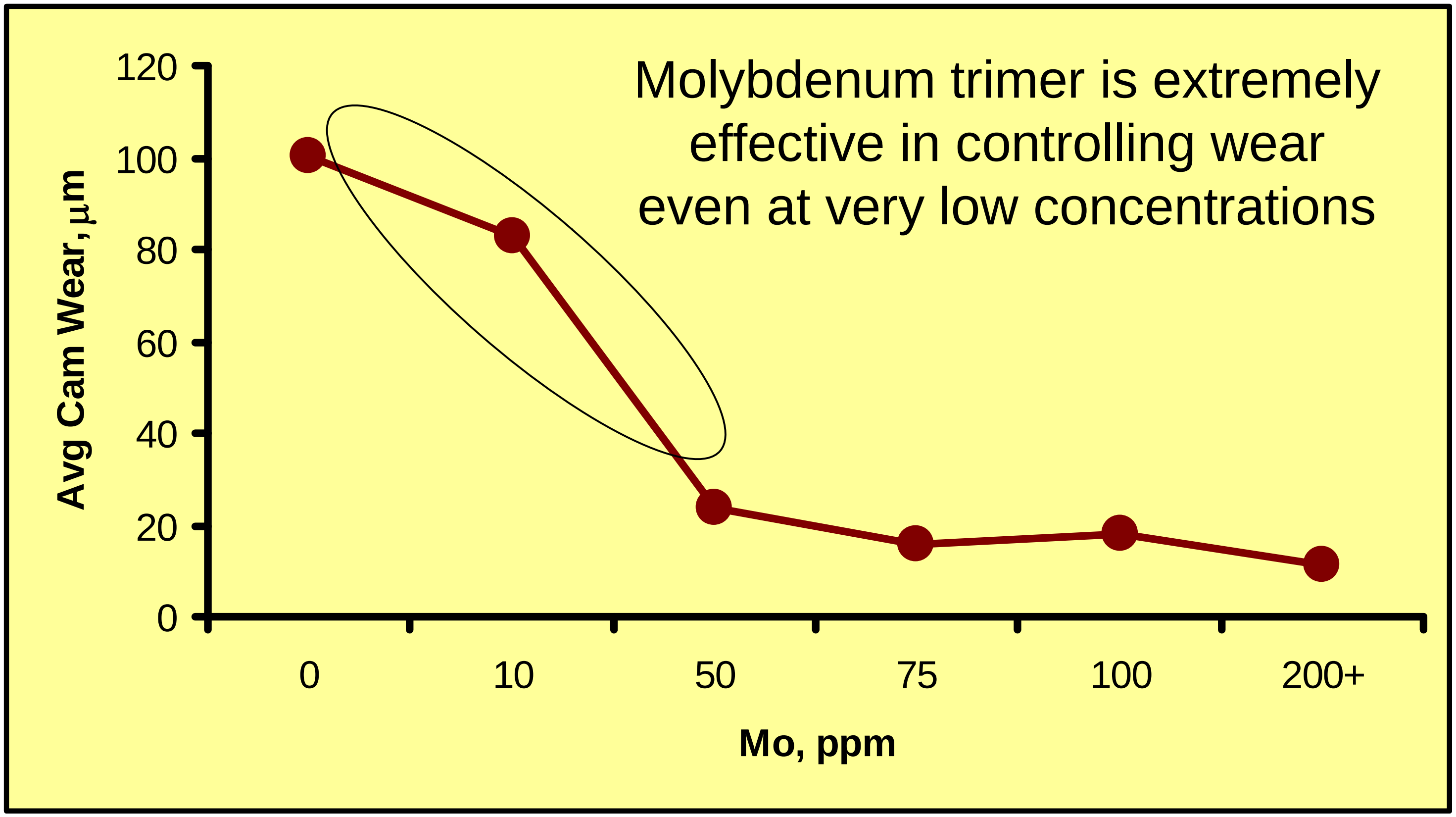
Molybdenum Trimer versus Sequence IV-A Cam Wear



Part 2: Molybdenum Trimer at Non-Conventional Material Contacts

Notes on Non-Conventional Contacts

- Commercial oils typically formulated for conventional contacts
- Recent emergence of non-conventional (non-ferrous) contacts in some engine designs
- Significant recent efforts at Infineum and with various research partners to determine friction and wear protection afforded by molybdenum trimer at non-conventional contacts
- Two non-conventional contact types will be considered
  - Steel-DLC
  - Steel-AluSil

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Steel-DLC

DLC Introduction: Basic Outline

- DLC coatings are made of carbon and have “diamond-like” properties
- Notable properties are hardness and low friction coefficient
  - Some DLC have “diamond like” hardness of 90GPa (diamond is 100 GPa)
- DLC can be metal doped providing better adhesion to a given substrate
- Manufactured mainly using CVD and PVD
- Classification of DLC is generally achieved with reference to
  - The ratio of sp^2/sp^3 hybridised carbon (the ratio is particularly important!)
  - The presence / absence of hydrogen in the matrix
  - The presence of doping elements such as Fe, W, Ti, Si or Cr
- Nomenclature
  - a-C:H hydrogenated DLC with H as high as 50%
  - a-C non hydrogenated DLC with H as low as 1 to 2%
  - ta-C tetrahedral hydrogen free DLC
  - ta-C:H tetrahedral hydrogenated DLC
- Difficult to translate the tribological behaviour of one coating to another

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Interactions of Molybdenum Lubricant Additives with DLC Coatings

- A number of studies of lubricant additives / DLC have been undertaken
- MoS_2 has been observed at DLC surfaces
- Mechanism for deposition may be different to that observed at ferrous contacts
- ZDDP & Mo-DTC operate synergistically
- M.I. de Barros Bouchet *et al*. (2005)
  - Mo-DTC and ZDDP react on DLC coatings
  - Higher reactivity on selected hydrogenated (over non-hydrogenated) DLC
- A. Neville (2007)
  - Mo-DTC give MoS_2 on DLC surfaces
  - Good correlation between MoS_2 / MoO_3 ratio and friction performance

(1) M.I. de Barros Bouchet, J.M. Martin, T. Le-Mogne & B. Vacher; “Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives” Tribology International 38 (2005) 257-264

(2) T. Haque, A. Morina, A. Neville, R. Kapadia, S. Arrowsmith; “Non-ferrous coating / lubricant interactions in tribological contacts: assessment of tribofilms” Tribology International 40 (2007) 1603-1612

Molybdenum Trimer Durability Benefits with DLC Coatings

- Experimental set-up used
  - Hydrogenated DLC coated plate on steel and cast iron counterbody
  - Pin-on-plate test rig
  - PAO base oil and different additive used
    - primary/secondary ZDDP alone or with molybdenum dimer / trimer
- Poor coating durability for PAO / ZDDP or PAO / Mo-DTC alone
- Enhanced coating durability for ZDDP / molybdenum dimer & trimer
  - Formation of molybdenum disulphide at the surface of the wear track (XPS)
- Absence of phosphorus at the surface but presence of Zn, ZnO, ZnS indicate a different mechanism of ZDDP decomposition at the surface and wear protection

(1) Haque, Morina, Neville, Kapadia, Arrowsmith; “Effect of oil additives on the durability of hydrogenated DLC coating under boundary lubrication conditions” Wear 266 (2009) 147-157 (Infineum-supported research)

Molybdenum Trimer Durability Benefits with DLC Coatings

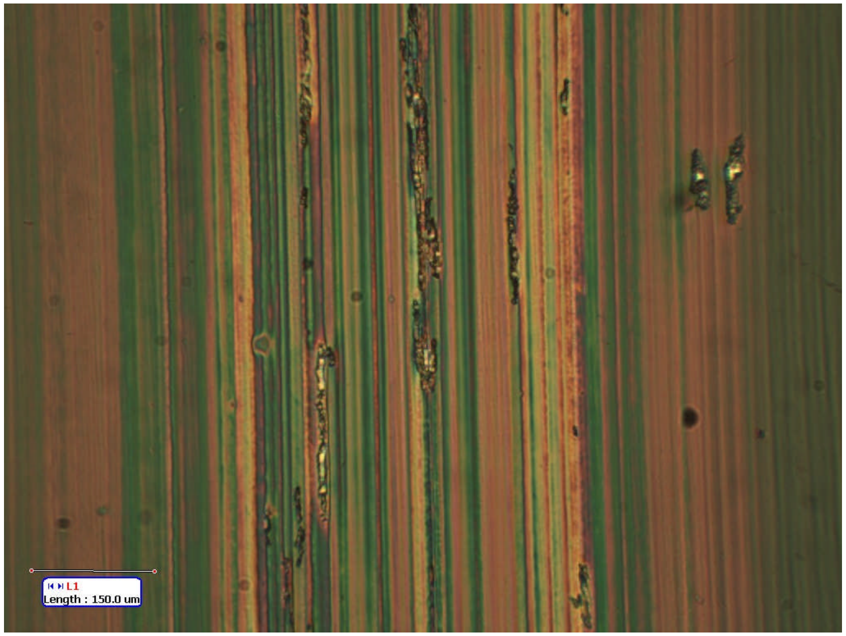
- ZDDP / molybdenum trimer gave durability benefits over molybdenum dimer
  - Pin wear H-DLC/CI 9.45×10^{-19} (dimer) / 4.76×10^{-19} (trimer)
- Microscope images of the wear scar on DLC coating for ZDDP / molybdenum dimer & trimer oils show significantly reduced delamination
- Molybdenum dimer oil shows some delamination along the wear track
- Durability of the DLC largely influenced by ZDDP-molybdenum-DTC synergy
- Synergy strongest for molybdenum trimer

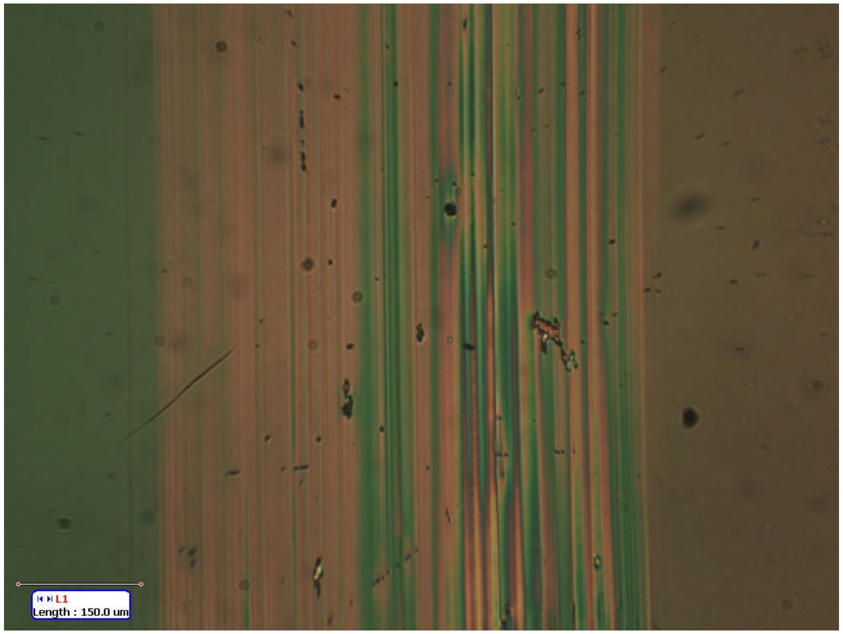
(1) Haque, Morina, Neville, Kapadia, Arrowsmith; "Effect of oil additives on the durability of hydrogenated DLC coating under boundary lubrication conditions" Wear 266 (2009) 147-157 (Infineum-supported research)

Molybdenum Trimer Durability Benefits with DLC Coatings

- Molybdenum Dimer / ZDDP

Molybdenum Trimer / ZDDP





- Length – 150 μm (microscopic images)

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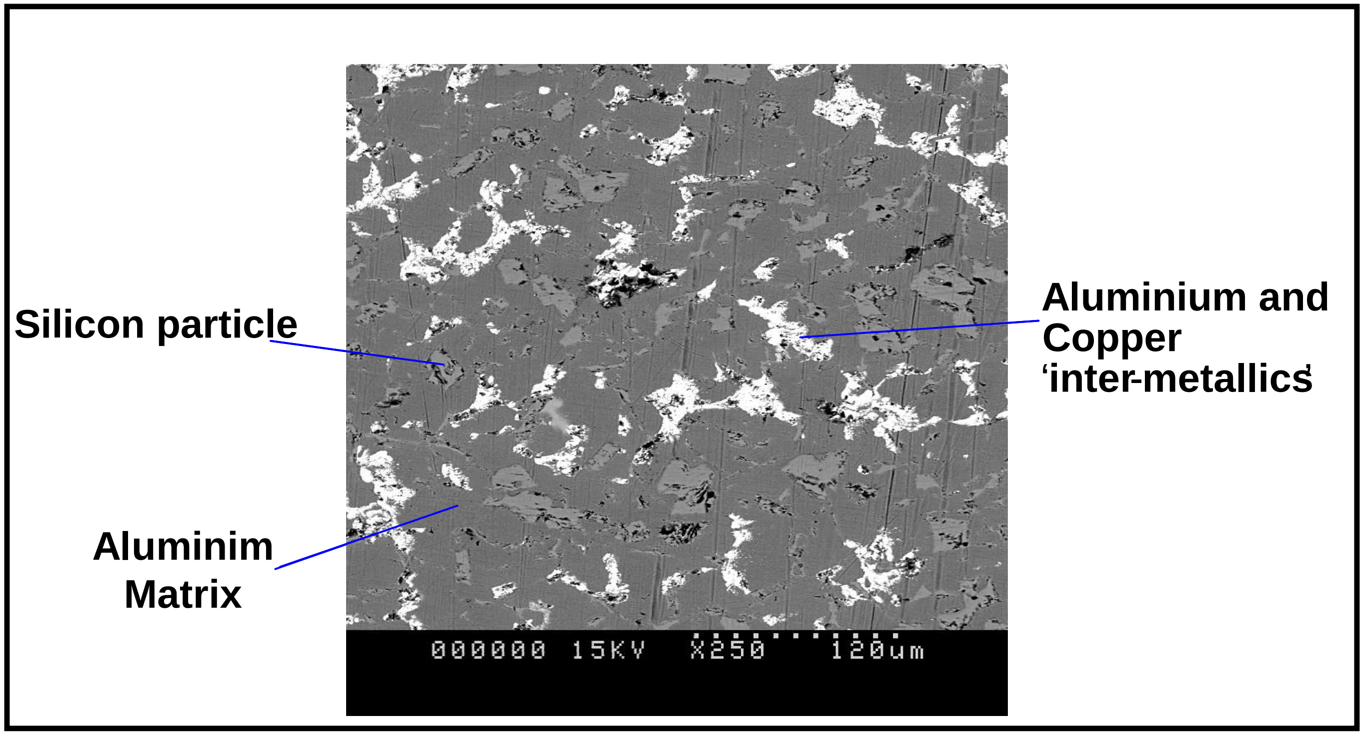
Steel-Alusil^{TM}

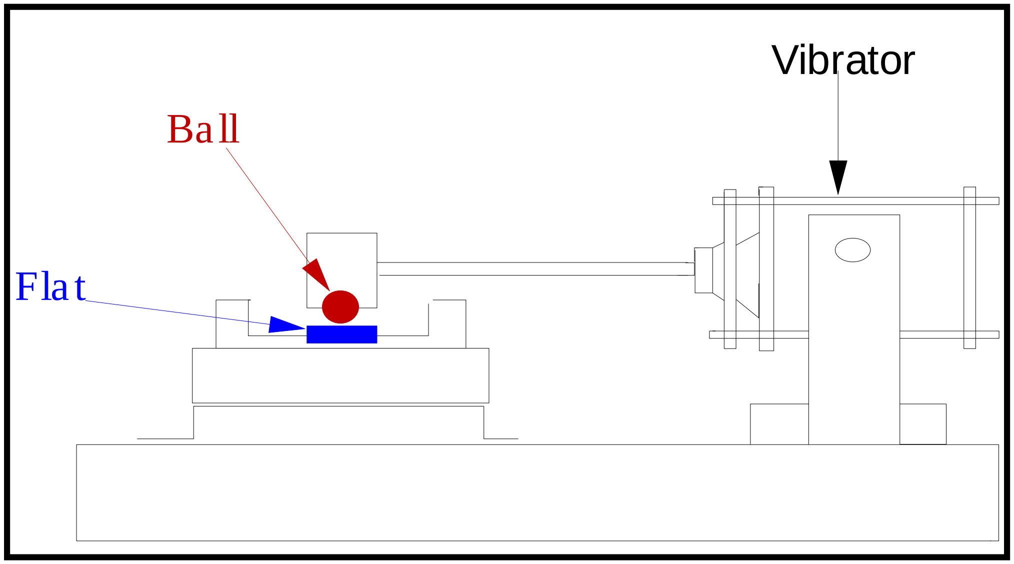
What is Alusil^{TM}?

- Alusil^{TM} is a trade name for a hypereutectic aluminium-silicon alloy ($AlSi_{17}Cu_4Mg$) with a silicon content of 16-18%.
- Alusil^{TM} cylinder liners give a significant weight saving over iron options

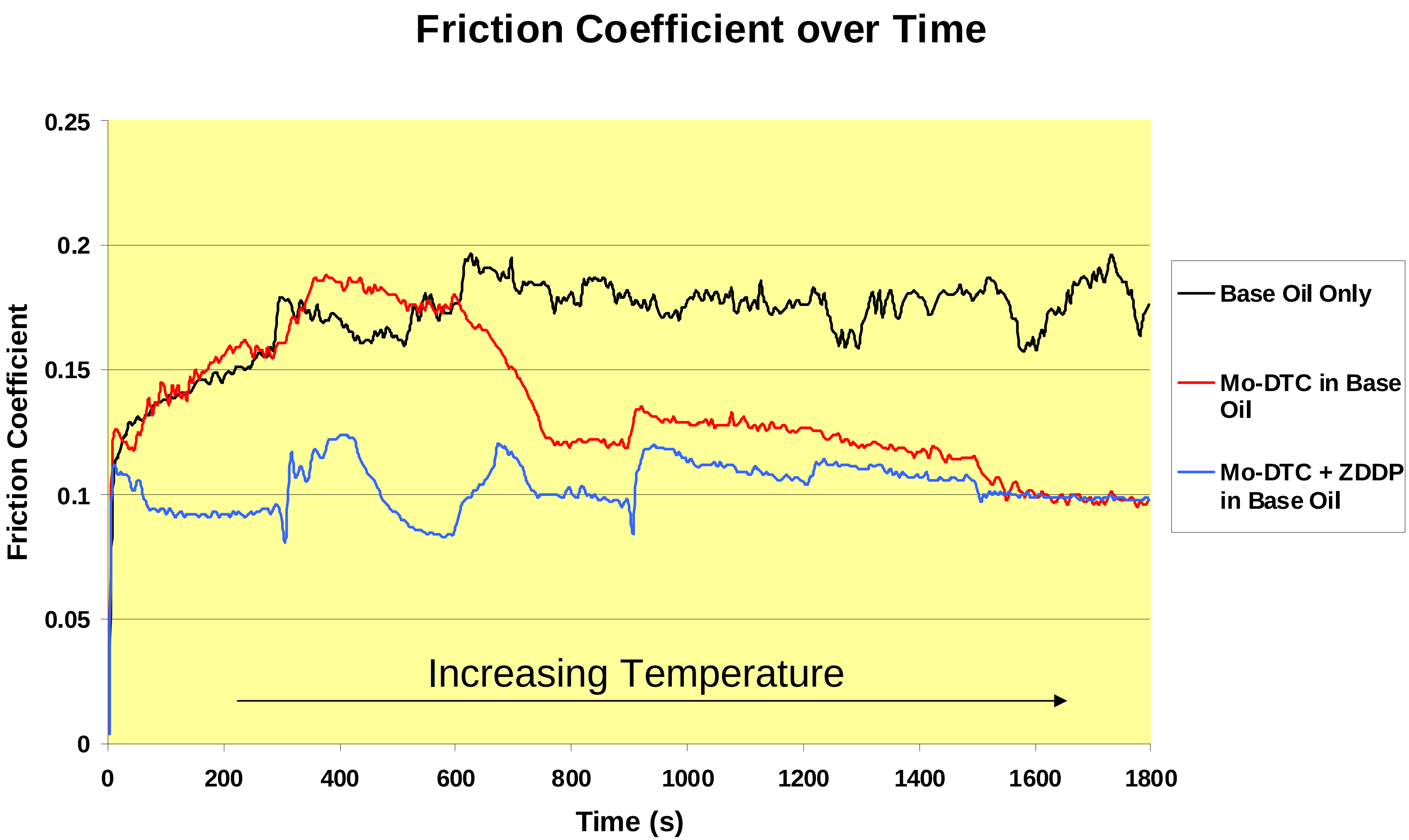


Test Method Development for Friction and Wear

- Modified HFRR substrates produced to give steel (ball) on Alusil™ (disc) contact mimicking ring-on-liner interface
- HFRR run at constant temperature to generate friction trace and deposit tribofilm
- XPS data collected from HFRR wear scar after test completed



Steel-Alusil^{TM} HFRR (1)



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Steel-Alusil™ HFRR (2) – Further HFRR Experiment

- Molybdenum dimer & trimer comparison
- Mo-dimer shows low to high friction coefficient changes over test
- Test stopped: XPS analysis of substrates gives surface composition
- Surface concentration of Mo & S higher for molybdenum trimer

Atom %	Molybdenum Trimer	Molybdenum Dimer (Low Friction)	Molybdenum Dimer (High Friction)
Molybdenum	8.2	5.6	2.6
Sulfur	6.2	4.7	2.8

Atom %	Molybdenum Trimer	Molybdenum Dimer (Low Friction)	Molybdenum Dimer (High Friction)
Mo(IV)	4.5	2.7	1.1
Mo(VI)	3.8	2.9	1.5

Conclusions

- Tribology and engine test data have been presented for molybdenum trimer in four contact environments
  - "Conventional" (bench and engine)
  - Steel-DLC
  - Steel-AluSil™
- Molybdenum trimer affords reduction in wear and friction
- Low wear rates seen an industry standard engine wear test even at very low molybdenum treat-rates (Seq. IVA)
- Friction reduction has been seen at a steel-steel contact (HFRR)
  - Molybdenum trimer best performing additive tested
- Friction reduction, durability improvements and molybdenum disulfide deposition have been shown for unconventional contacts

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Acknowledgements

- Alusil™
  - Infineum Crankcase Development Team: Paul Symmers & Nigel Broom
  - BP Product Research Team: Marc Payne, Hugh Preston & Chris Warrens
- DLC
  - Leeds University: Anne Neville, Tabassamul Haque
  - Infineum Components Development Team: Steve Arrowsmith & Rita Kapadia

DLC: Infineum Involvement & Publications

1. PhD Theses

- *"Optimisation of crankcase lubricant additive – material combinations for reduced friction and wear in internal combustion engines"*, Heriot-Watt University, May 2005
- *"Tribochemistry of lubricant additives on non-ferrous coatings for reduced friction, improved durability and wear in internal combustion engines"*, Leeds University Dec 2007

2. Publications

- *"Non-ferrous coating/lubricant interactions in tribological contacts: Assessment of tribofilms"* Tribology International, Volume 40, Issues 10-12, October-December 2007, Pages 1603-1612
- *"Study of the ZDDP antiwear tribofilm formed on the DLC coating using AFM and XPS techniques"*, Journal of ASTM International 4 (2007), pp. 0–7 (online)
- *"Effect of oil additives on the durability of hydrogenated DLC coating under boundary lubrication conditions"*, Wear, Volume 266, Issues 1-2, 5 January 2009, Pages 147-157

3. Patents

- SG 125947 (A1), EP 1462508 (A1)
  A method of lubricating a surface coated with a diamond-like carbon film or coating which comprises supplying to said surface a lubricating oil composition comprising an oil of lubricating viscosity and an effective friction reducing amount of an oil soluble organo-molybdenum compound.

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