



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

Reproduction of any material whether by photocopying or storing in any medium by electronic means or otherwise is prohibited without prior written consent of Infineum International Limited.

© Copyright INFINEUM INTERNATIONAL LIMITED 2009. All rights reserved

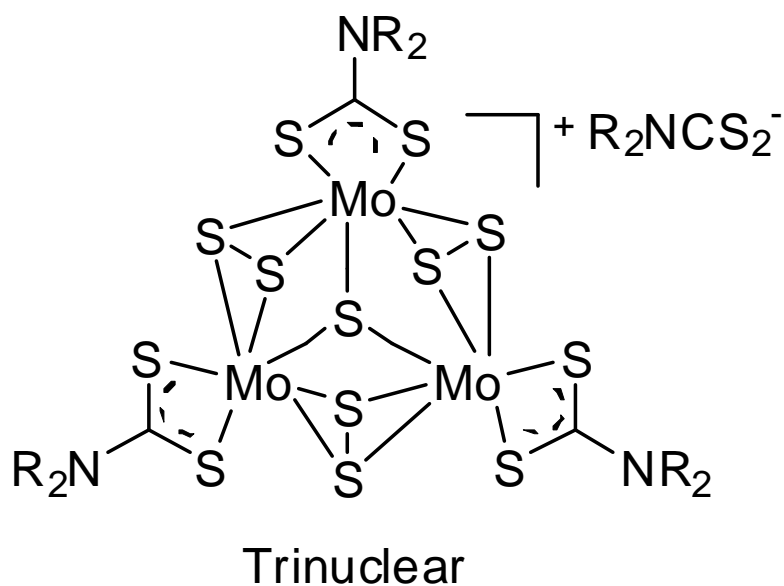
See the legal disclaimer notice on www.infineum.com

"INFINEUM", "DOBANAX", "PARATAC", "SYNACTO", "VEKTRON", and the corporate mark comprising the interlocking ripple device are trademarks of Infineum International Ltd. "VISTONE" is a trademark of Exxon Mobil Corporation used under licence by Infineum International Limited.

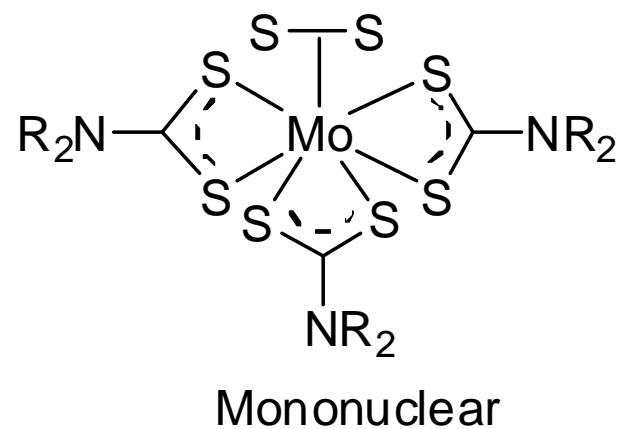
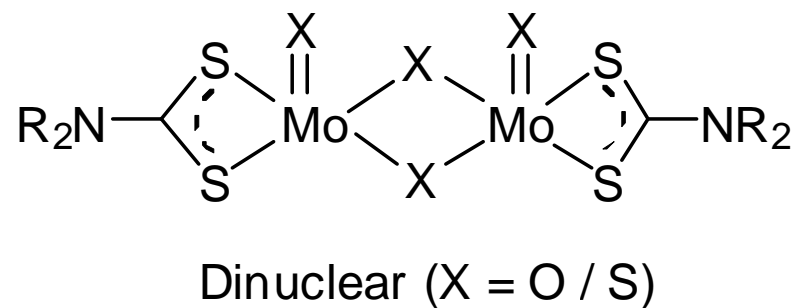
Outline

- 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

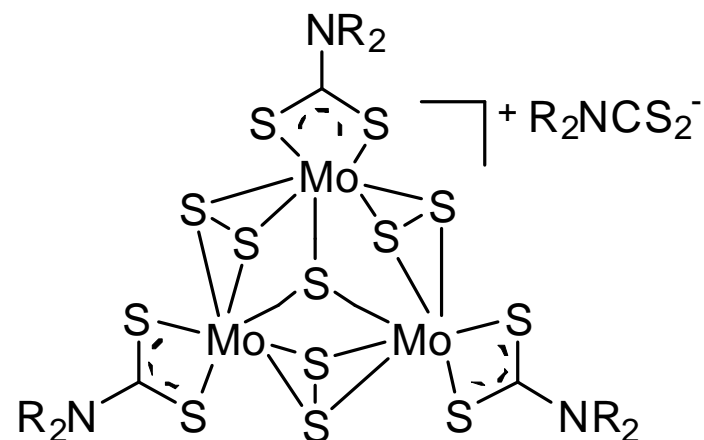


R = hydrocarbyl



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

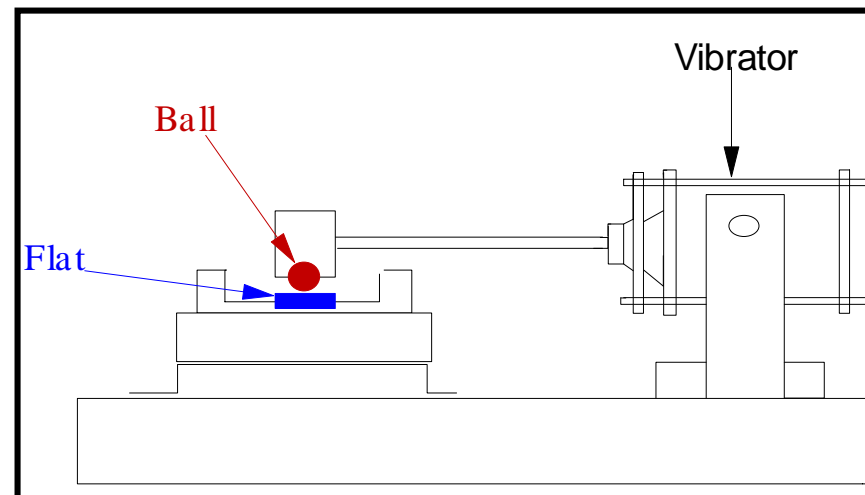


Trinuclear
R = hydrocarbyl

Part 1: Molybdenum Trimer at Conventional Material Contacts

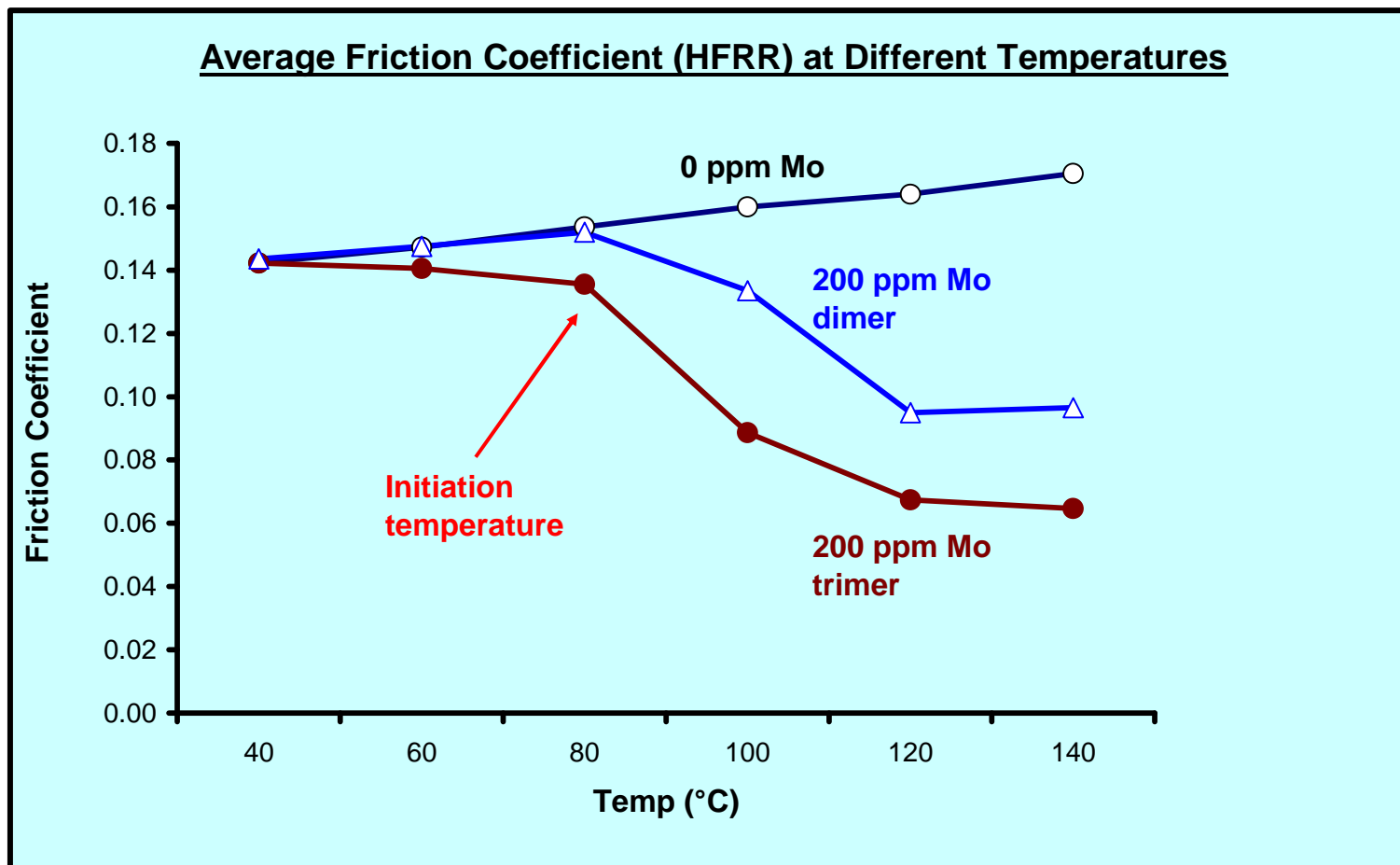
Introduction to HFRR Methodology

- 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



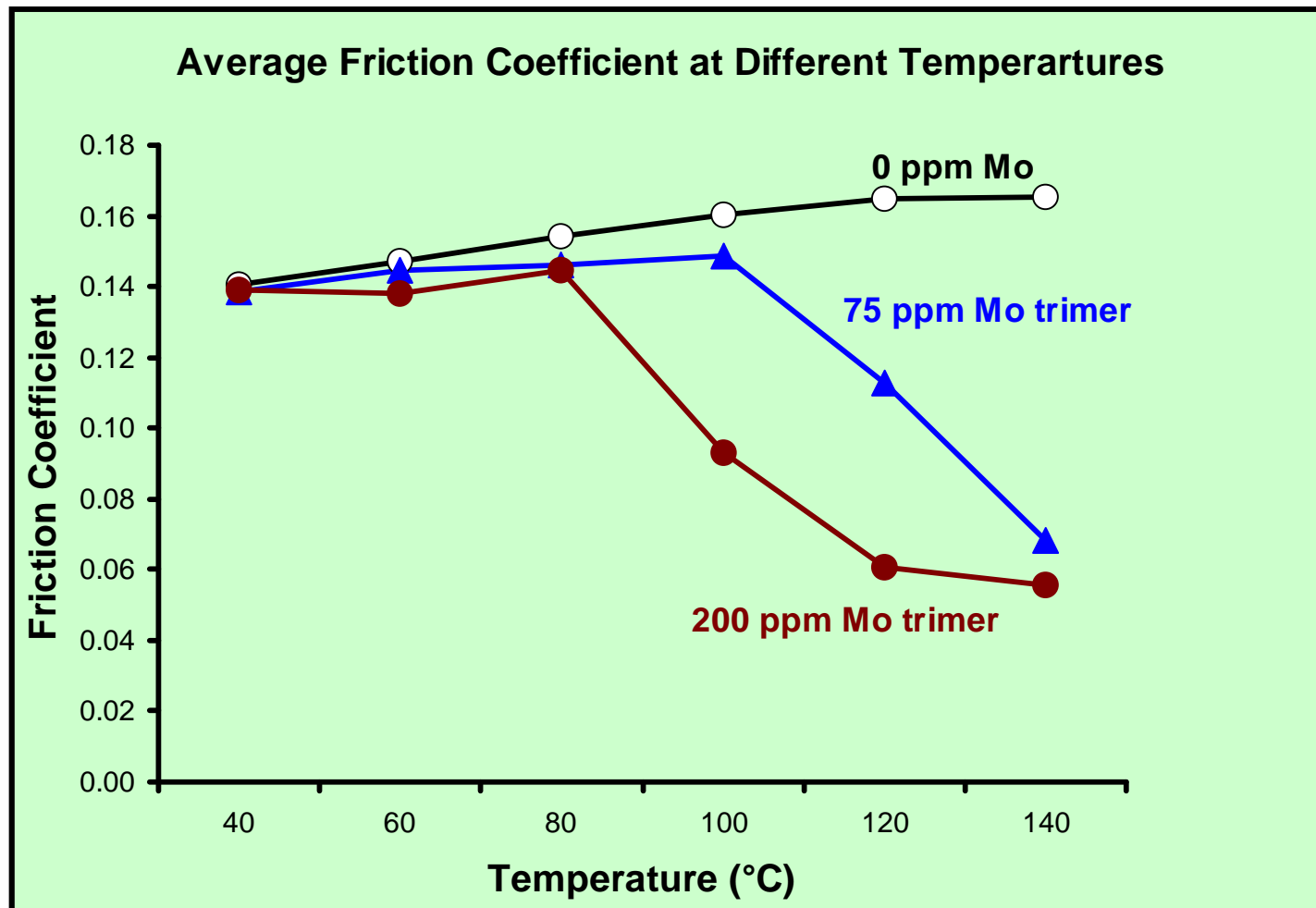
Steel on Steel: HFRR (2)

- 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

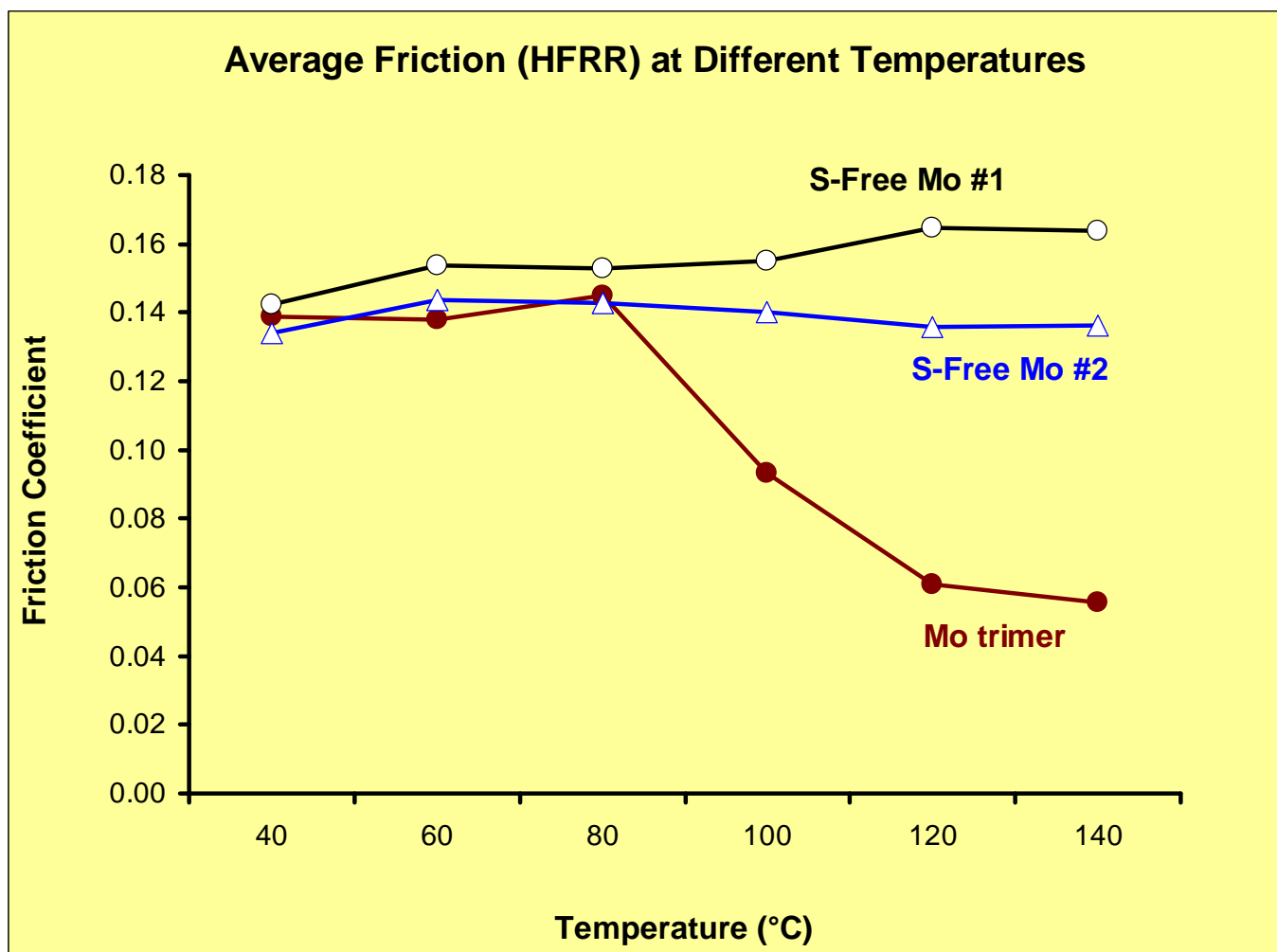
Steel on Steel: HFRR (3)

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



Steel on Steel: HFRR (4)

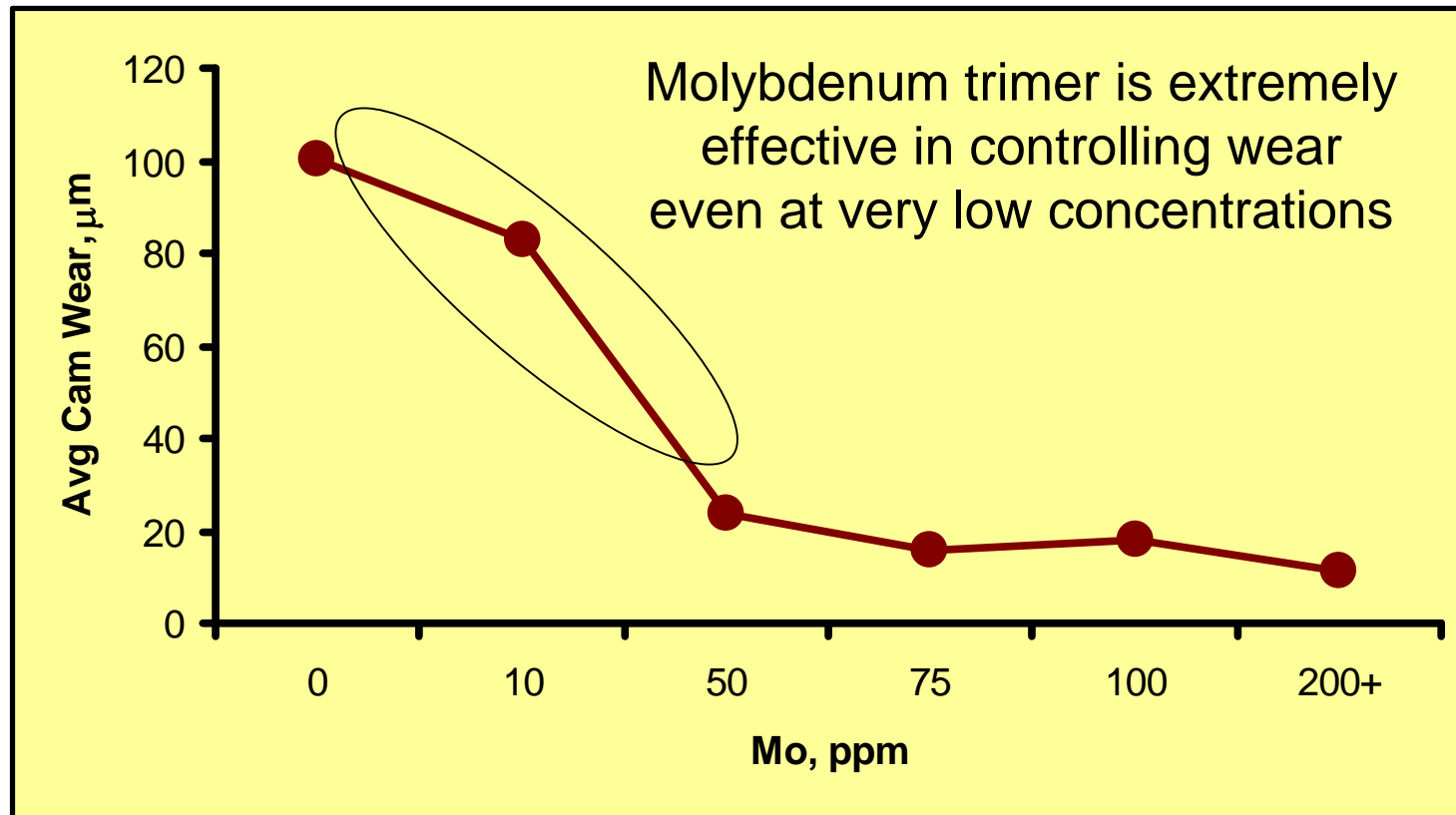
Sulphur-free molybdenum species show much higher friction coefficients



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

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

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

Interactions of Molybdenum Lubricant Additives with DLC Coatings

- A number of studies of lubricant additives / DLC have been undertaken
 - MoS₂ 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 MoS₂ on DLC surfaces
 - Good correlation between MoS₂ / MoO₃ 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

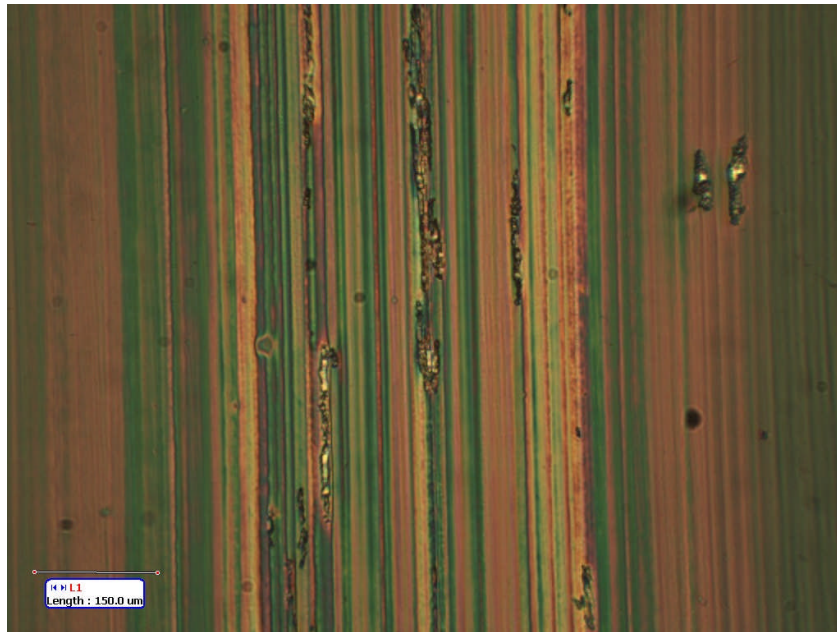
(1) Haque, Morina, Neville, Kapadia, Arrowsmith; “Effect of oil additives on the durability of hydrogenated DLC coating under boundary lubrication conditions” Wear 266 (2009) 147-157 (Infineum-supported research)

Molybdenum Trimer Durability Benefits with DLC Coatings

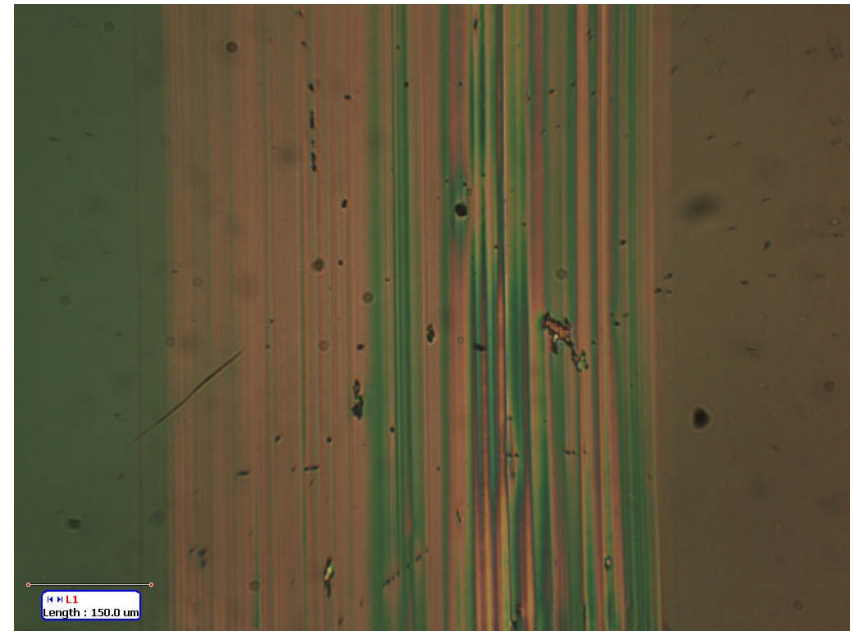
- ZDDP / molybdenum trimer gave durability benefits over molybdenum dimer
 - Pin wear H-DLC/CI 9.45×10^{-19} (dimer) / 4.76×10^{-19} (trimer)
 - Microscope images of the wear scar on DLC coating for ZDDP / molybdenum dimer & trimer oils show significantly reduced delamination
 - Molybdenum dimer oil 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

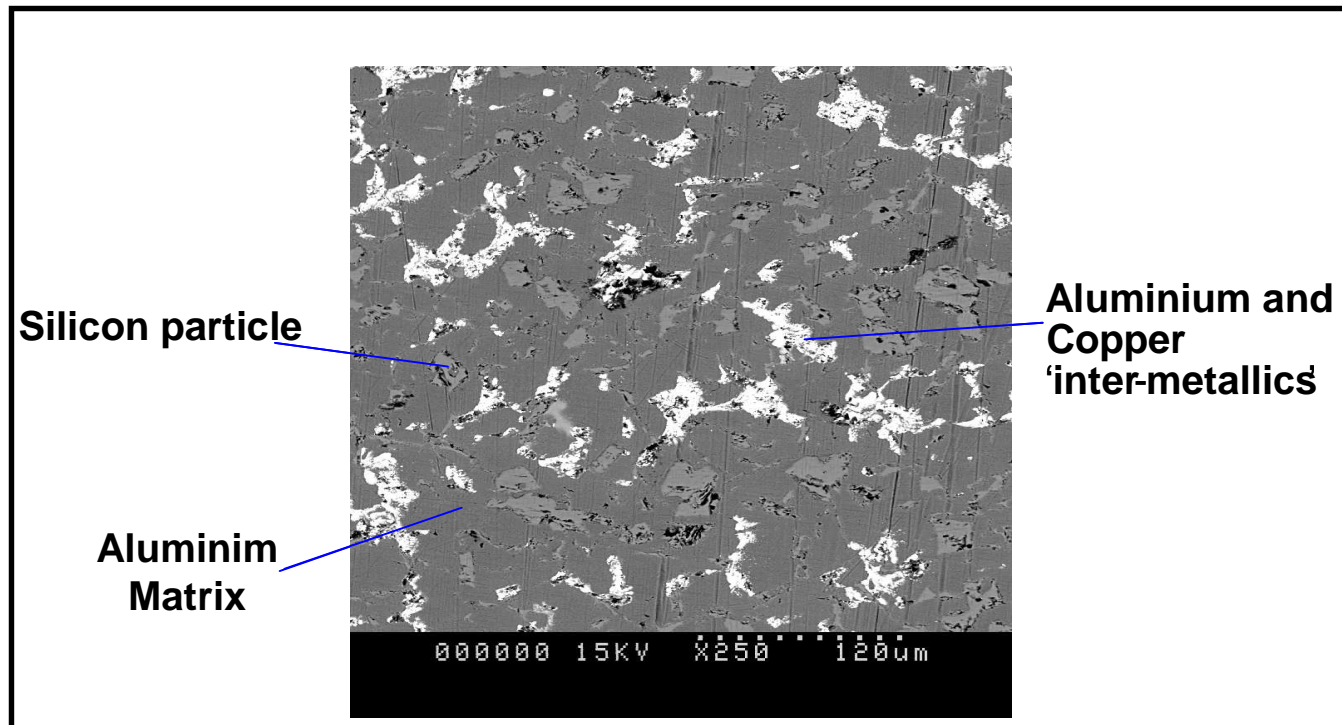


○ Length – 150 μm (microscopic images)

Steel-Alusil™

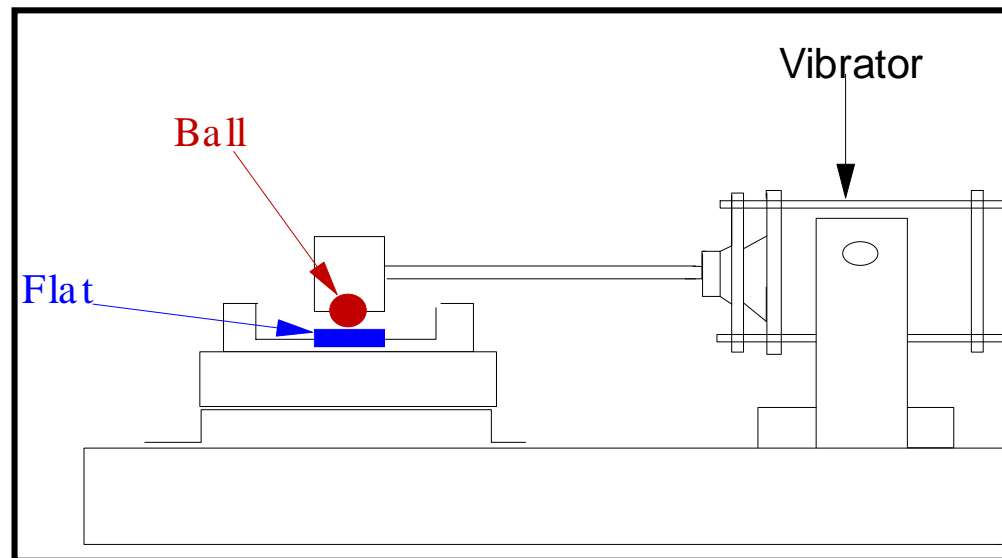
What is Alusil™?

- Alusil™ is a trade name for a hypereutectic aluminium-silicon alloy ($\text{AlSi}_{17}\text{Cu}_4\text{Mg}$) with a silicon content of 16-18%.
- Alusil™ cylinder liners give a significant weight saving over iron options



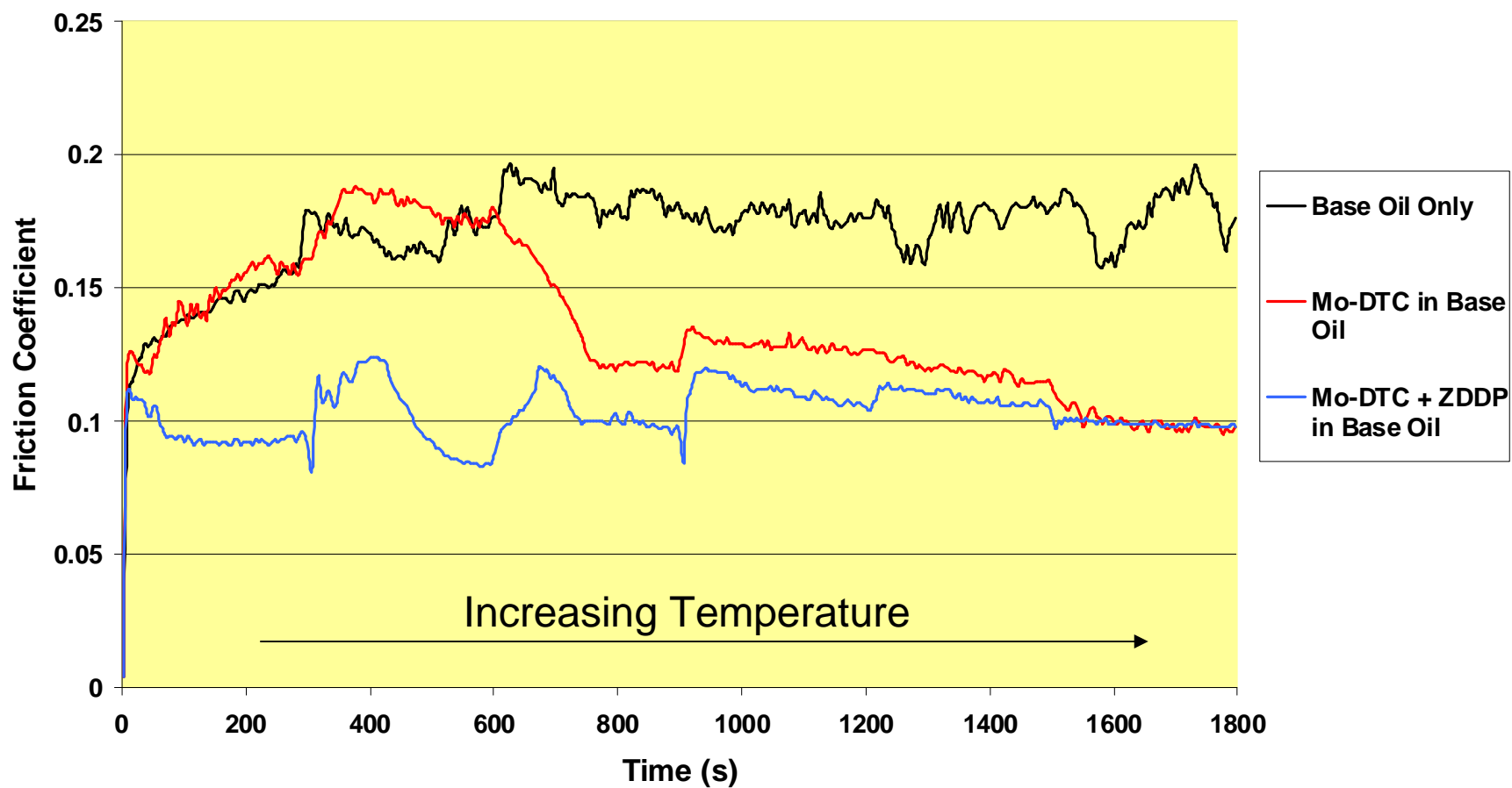
Test Method Development for Friction and Wear

- 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-Alusi™ HFRR (1)

Friction Coefficient over Time



Steel-AlusiTM 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

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.

