Smart electromagnetically responsive nanoadditized lubricants

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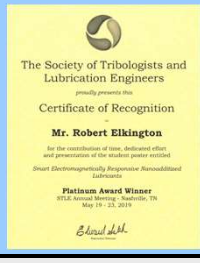


Introduction

The current global lubrication challenges in the fields of energy, materials, transportation and manufacturing require smart solutions which can also fulfil the enormous safety, environmental demands and the governmental regulations for emission standards and fuel efficiency.

In transportation, the modern need for electric vehicles and sustainable transport presents a new set of lubricant challenges requiring green lubricants which have smart tribological properties, often with contradictory requirements. For example, Hybrid Electric Vehicles are subjected to multiple start-stop events and therefore average operating engine temperature are lower. Using a lower viscosity lubricant to facilitate engine start-up increases wear. In Battery Electric Vehicles lubrication can be affected by electric currents and strong electromagnetic fields and while apparently lubrication requires less attention, most electric motors fail due to the failure of 'permanently lubricated bearings'. This places new demands on gear oils, greases and coolants.

The solution is to develop a smart responsive green additive which can replace the polluting and ash-forming ZDDP antiwear additive while instantaneously providing superior wear and friction reduction at the required moment.

Tungsten disulphide nanoparticles (**2H-WS_2**) are the ideal candidate for lubricant additives. Their layered structure that exfoliates easily in tribological applications provides remarkable friction reducing properties while the ability to generate a chemical tribofilm in high temperature (T>50°C), high pressure conditions with very good mechanical properties gives excellent antiwear properties. 2H-WS_2 NPs generate chemical tribofilms with a similar thickness, morphology, and antiwear properties to ZDDP and ZDDP + organic friction modifier (OFM) films (Fig. 2), and unlike ZDDP, 2H-WS_2 NPs are able to instantly reduce friction in boundary lubrication (Fig. 1).

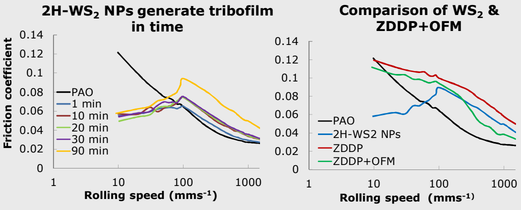


Figure 1: Comparison of 2H-WS2 NPs, ZDDP, ZDDP + OFM antifriction properties [1]

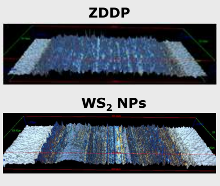


Figure 2: Profilometry images of WS2 and ZDDP additive tribofilms (z axis increased 30 times) [1]

Smart, instantly responsive nanoadditives can be achieved by doping WS_2 NPs with iron to induce magnetically susceptible behaviour and employing a local electromagnetic field around the tribological contact. This results in an increased concentration of NPs around the contact during challenging operating conditions leading to:

1. An increased rate of tribofilm generation and tailored antiwear/fricition reduction,
2. A lower optimal concentration of nanoadditive in base fluid and therefore improved stability of the colloid and reduced cost,
3. Recyclability of NPs.

Synthesis of Fe-doped WS_2 nanoadditive

Fe-doped 2H-WS2 (Fig. 3) have been synthetized in house by Fe-doping 2H-WS2 NPs in solution followed by air-annealing at 300°C. The magnetic properties of the NPs were characterised by measuring the magnetization versus magnetic field (Magnetic – Hysteresis) curves using a SQUID-VSM Magnetometer. Fe-doped NPs demonstrate little hysteresis and very low values for coercivity and remanence, indicative of *superparamagnetism* at ambient and engine operating temperatures (Fig. 4). Fe-doped WS_2 NPs therefore can produce strong induced magnetization in the presence of a EM field.

Two NPs dispersions in PAO (SpectraSyn Plus 3.6) were prepared using a probe sonicator:
1. **0.5 wt%** ferromagnetic WS_2 NPs
2. **0.15 wt%** ferromagnetic WS_2 NPs functionalized with oleate/oleic acid (Fig. 5)

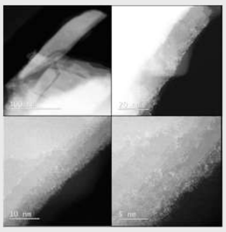


Figure 3: STEM images of iron oxide doped 2H-WS_2

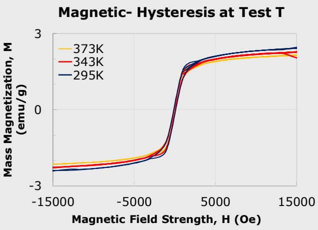


Figure 4: Magnetic – Hysteresis curves at 295 K, 343 K, 373 K in the range of -15000 Oe ≤ H ≤15000 Oe

Figure 5. Functionalized ferromagnetic 2H-WS in PAO

Testing methods

The influence of the electromagnetic field on the tribological performance of the nanoadditive was investigated using two types of WS2 NP dispersions in PAO base oil:
1. EHD tests were carried out with 0.5 wt.% NPs in the PAO oil
2. MTM tests used 0.15 wt.% NPs functionalised with oleate/oleic acid

Two set-ups were employed in the EHD to allow visualisation of the tribofilm development between a steel ball and the glass disc (Fig. 6 (a), Position 1) and to measure friction between the steel ball and steel disc. (Fig. 6 (a), Position 2). The EHD testing procedures are summarised in Table 1. Tribofilm development on wear tracks was analysed by optical microscopy and profilometry (Alicona).

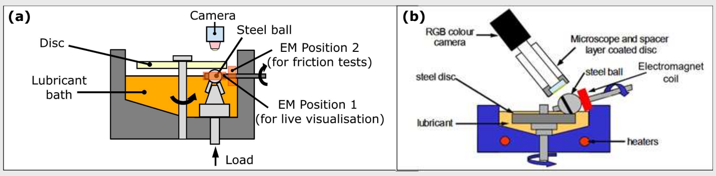


Figure 6: (a) Schematic of EHD Ultra-Thin Film Measurement System showing positions 1 and 2 of the EM coil, **(b)** Schematic of Mini Traction Machine (MTM) showing the position of the EM coil

Further tribological tests were carried out using the MTM-2 in a sliding-rolling ball-on-disc setup with the EM coil positioned behind the ball, Fig. 6 (b). The tribological tests ran for 3 hours and involved repeated conditioning phases and Stribeck measurements phases. The testing routine employed is summarised in Table 2.

Table 1. EHD testing conditions

	Tribofilm visualisation (Position 1)	Friction Measurement (Position 2)
EHD Contact	Ball and standard spacer layer disc	Ball and steel disc
Load/ MHP	20 N / 0.53 GPa	20 N / 0.82 GPa
Temperature	70 ±0.5 ˚C	70 ±0.5 ˚C
Speed	0.04 ms^{-1}	0.01-1.0 ms^{-1}
SRR	0%	50% and 100%
Time	10 min	10 min / 2 min (Stribeck)

Table 2. MT2 testing routine

	Conditioning Phase	Stribeck Phase
MTM Contact	Ball and steel disc	
Load / MHP	30 N / 0.94 GPa	
Temperature	80 ± 0.5 ˚C	
Speed	0.1 ms^{-1}	1.5 to 0.01 ms^{-1}
SRR	150 %	
Time	3 h	2 min

Results and Discussion

EHD Testing: Fig. 7 shows the generation of the wear track tribofilm is accelerated in the presence of an EM field, as indicated by the noticeably darker, and hence thicker, more uniform tribofilm when the EM is ON. This effect is achieved by attracting the NPs to the weakly magnetized ball and thus increasing the concentration of WS_2 in the contact inlet.

Friction in the boundary/mixed lubrication regime, Fig. 8 (a), displays a friction drop of 15% in pure sliding (100% SRR) and 11% at a low (50%) SRR. Stribeck curves, Fig. 8 (b), in pure sliding demonstrate NPs reduce friction in all lubrication regimes under the influence of an EM field. Optical micrographs, Fig. 8 (c), and profilometry investigation of the steel disc wear track show a thicker and more uniform tribofilm is formed under the influence of an EM field.

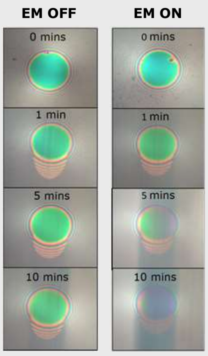
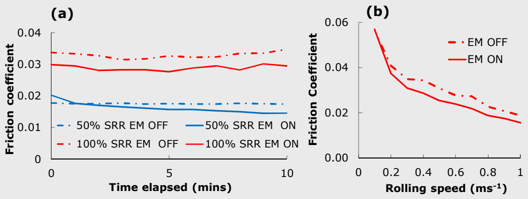


Figure 7: Interferometry images of the EHD contact lubricated with responsive 0.5 wt.% WS_2 NPs in PAO. The sliding direction is top to bottom



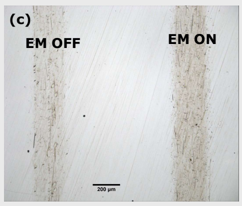


Figure 8 (a) Friction coefficient vs. time in boundary/mixed lubrication regime (constant speed 40 mms^{-1}) at 70 °C at 50% and 100% SRR with EM ON/OFF
(b) Stribeck curves at 70 °C and 100% SRR with EM ON and OFF
(c) Optical micrographs of the tribofilms generated on the steel disc tracks after 10 minutes of pure sliding with EM ON/OFF

MTM Testing: The Stribeck curves, Fig. 9, show that under the influence of an EM field the WS_2 tribofilm forms notably quicker than with EM OFF. This is due to the increased concentration of NPs in the contact. The higher friction with EM ON is attributed to the formation of a comparatively thicker tribofilm due to the increased concentration of NPs in the contact and accelerated film formation.

Profilometry measurements show a more uniform and thicker tribofilm for EM ON (average thickness 192 nm, Fig. 10 (b)) than EM OFF (average thickness 125 nm, Fig. 10 (a)).

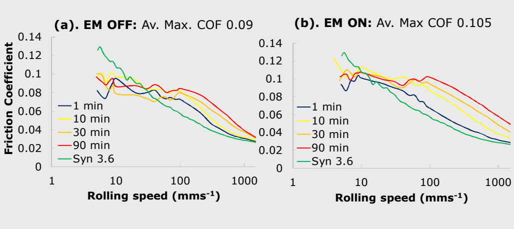


Figure 9: Stribeck Curves for Syn3.6 and Syn3.6 + 0.15 wt% WS2 NPs after 1, 10, 30, 90, and 180 minutes of rubbing with **(a)** EM OFF and **(b)** EM ON

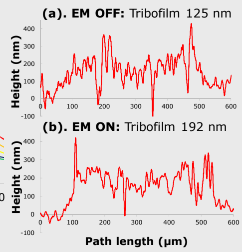


Figure 10: Profile across wear track **(a)** with EM OFF, **(b)** with EM ON

Conclusions

Advancements in nanotechnology and colloidal chemistry allow the synthesis of smart electromagnetically responsive 2H-WS_2 NPs which can enable:

1. Instant control of the rate of tribofilm formation on wear track during demanding operations by increasing NPs concentration in tribological contact which results in a protective/healing effect,
2. Ability to manipulate lubricant performance i.e. increased wear protection/higher friction or lower friction/reduced wear protection,
3. Replacement of problematic antiwear additive ZDDP with a nanoadditive which beside having superior tribological properties is ashless and environmentally friendly,
4. Reduction of the optimal concentration of NPs, making them more cost efficient
5. NPs recyclability.

References:

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Ratoi, M., Niste, V.B., Walker, J., Zekonyte, J., Mechanism of action of WS_2 lubricant nanoadditives in high-pressure contacts. *Tribology Letters*, 52, pp. 81-91, (2013)

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