



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/148631/>

Version: Accepted Version

Article:

Khan, T, Tamura, Y, Yamamoto, H et al. (2019) Tribological response of MoS₂ coated and oxy-nitrided samples with alternative extreme pressure and anti-wear additives.

Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 233 (8). pp. 1256-1273. ISSN: 1350-6501

<https://doi.org/10.1177/1350650119829390>

This article is protected by copyright. This is an author produced version of an article published in Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Tribological response of MoS₂ Coated and oxy-nitrided samples with alternative extreme pressure (EP) and anti-wear (AW) additives

Thawhid Khan^{1)*}, Yukio Tamura²⁾, Hiroshi Yamamoto²⁾, Anne Neville¹⁾ and Ardian Morina¹⁾

¹⁾ Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, United Kingdom

²⁾ Materials Technical Centre, Development Division, Komatsu Ltd., Kanagawa 254-8567, Japan

*Corresponding author: T.A.Khan@leeds.ac.uk

Oxy-nitriding (QPQ) and MoS₂ coatings are widely used surface modification techniques in industry to improve the friction and wear characteristics of components and interacting surfaces. To ensure optimum performance of components within tribological environments it is crucial to ensure compatibility between surfaces and lubricants, as the break-down of the lubricating film could lead to seizure between interacting components. This study analyses the interaction of extreme pressure and anti-wear additives with two modified surfaces. The friction and tribofilm formation behaviour were investigated using a Mini Traction Machine (MTM2) fitted with a 3D Spacer Layer Imaging Method. The chemical composition of the species formed after testing was analysed using X-ray Photoelectron Spectroscopy (XPS). This study found that the properties of the modified surfaces and their interaction with the various lubricant additives impact their tribological performance. With the oxy-nitrided samples no real effect on friction was observed when using the Sulphurised Olefin (SO) or Tricresyl Phosphate (TCP) additives, mostly due to lack of interaction with the less reactive iron nitride layer and their roles as anti-wear additives. However when using the SO additive with the MoS₂ coated sample, a significant reduction in friction was observed with time. This was mostly likely due to the combined effect with formation of FeS and MoS₂ within the tribofilm.

Keywords: tribology, tribochemistry, coatings, heat treatments, additives

1. Introduction

Hydraulic motors/pumps are key components within hydraulic systems, but they are hindered by their inefficiency which in some cases can be up to 15% [1]. High friction between interacting components can cause excessive wear and may also initiate seizure and complete failure of the motor/pump [2].

The application of heat treatments and coatings on steel surfaces is an effective way to improve the tribological properties of steel. This improvement can be further enhanced through ensuring the compatibility between the treated surface and lubricants within tribological environments. The role of surface protective additives is crucial with severe operating conditions and moving components in the boundary lubrication regime. Through the tribochemical reaction of the additives at the contact a protective film can be formed. The nature of this film and the regeneration of the protective layer are dependent on the presence

1 of the additive package [3, 4, 5]. There is still much to be learnt about surface/lubricant
2 interactions when the surfaces have been exposed to heat-treatment or surface engineering.

3 The use of various extreme pressure and anti-wear additives to base lubricants is a common
4 and effective method to reduce friction and wear. The lubrication behaviour of the additive is
5 influenced by the properties of the interacting surfaces, the environmental atmosphere and the
6 properties of additive itself. Zinc dialkyldithiophosphate (ZDDP) is one of the most successful
7 and effective anti-wear and extreme-pressure additives commonly applied to hydraulic fluids.
8 The formation of a glassy sacrificial phosphate film at interacting contacts helps determine
9 the effectiveness of the wear reduction though preventing adhesion between surfaces and
10 reducing stresses caused by surface asperities. The interaction of ZDDP with solid surfaces
11 often leads to the formation of different compounds such as iron sulphide or zinc/iron
12 phosphate which could further impact the wear and friction behaviour of the tribofilm [6]. On
13 steel samples, the tribofilms can grow to a thickness >100 nm and have an uneven pad-like
14 structure [7]. Previous work showed oxy-nitrided (QPQ) samples performed tribologically
15 better than untreated and coated samples during tribometer tests in terms of friction and wear,
16 when fully formulated hydraulic oil was used as a lubricant [6].

17 Alternative extreme pressure and anti-wear additives to ZDDP include sulphurised olefin
18 (SO) and tricresyl phosphate (TCP), which are both widely used within industry. The
19 effectiveness of SO as an extreme pressure additive is due to the formation of a film of
20 sulphide covering the metal surface [8]. FeS is softer than the metal surface and behaves as a
21 solid lubricant. Sulphur additives are deemed highly effective in the most severe operating
22 conditions and help to mitigate scuffing [9].

23 TCP demonstrates good anti-wear behaviour due to its chemical reaction with iron to form an
24 iron phosphate and iron oxide film. Phosphorous containing compounds are effective anti-
25 wear additives under moderate friction conditions and allow the application of higher loads
26 [8]. Several researchers [10] have indicated that the effectiveness of SO and TCP additives
27 are determined by the presence of oxygen in the testing atmosphere.

28 The aim of this project is to investigate the chemical interactions with various EP additives
29 and treated surfaces in different lubrication regimes. The interaction between an oxy-nitrided
30 and MoS₂ coated steel surface and hydraulic oils containing alternative EP and AW additives
31 will be investigated. By using two alternative lubricant mixtures which were composed of
32 either sulphur or phosphorous containing additives, allowed the investigation of the effect of
33 both elements on the tribological behaviour of the treated surfaces individually. The goal of
34 the project is to achieve sustained low friction and wear behaviour through the optimisation
35 of these additive packages with a modified surface.

36 **2. Experimental Methodology**

37 The treated samples were lubricated with the different oil additives; two extreme pressure and
38 anti-wear additives widely used in industry – sulphurised olefin and tricresyl phosphate. The
39 use of sulphur and phosphorous based additives respectively would allowed the investigation
40 in to the interaction mechanisms of the treated samples with the different additives.

41 **2.1 Tribometer Testing**

1 A Mini Traction Machine (MTM2) tribometer (*Figure 1*) was used to measure the friction
2 and wear properties of the surface treatments with the oils containing different additives, with
3 the generation and composition of the tribofilms being investigated using the 3D Spacer Layer
4 Imaging Method (MTM-SLIM). The MTM tribometer allows the imaging of the formation
5 of a tribofilm with time on two different treated surfaces which have either been coated or
6 heat treated. It also allows the application of a sliding contact interacting within different
7 lubrication regimes which closely represents the movement occurring between components
8 within a hydraulic motor.

9 Using a Mini Traction Machine (MTM2) with a ball-on-disc configuration to represent the
10 sliding conditions of interacting components, the friction and wear behaviour of the treated
11 samples could be investigated. This set-up featured a $\frac{3}{4}$ inch ball made from nitriding steel
12 and treated as described above. The counter face was a 46 mm diameter disc composed from
13 spheroidal graphite cast iron which had been gas nitrided (650-670 HV₁). New specimens
14 (balls and discs) were used for each test and were cleaned with solvents in an ultrasonic bath
15 for 15 minutes prior to testing. During testing, the temperature was kept constant at 80°C and
16 a load of 36N was applied corresponding to an initial Hertzian contact pressure of 1 GPa. The
17 sliding-rolling ratio (SRR), defined as the ratio of the sliding speed ($U_b - U_d$) to the entrainment
18 speed $(U_b + U_d)/2$ (where U_b and U_d are the speed of the ball and the disc, with respect to the
19 contact) was 150% [7]. Yamaguchi [11] states the piston and cylinder component within the
20 piston pump is a pure sliding contact, but for this study a percentage of rolling contact will be
21 applied to replicate the rotation of the pistons within the cylinder block. The MTM2 is fitted
22 with 3D Spacer Layer Imaging Method (SLIM) attachment, which enables in situ capture of
23 optical interference images of the tribofilms on the steel ball. Using these images the
24 behaviour of the formation of a tribofilm on the different treated surface can be understood.

25

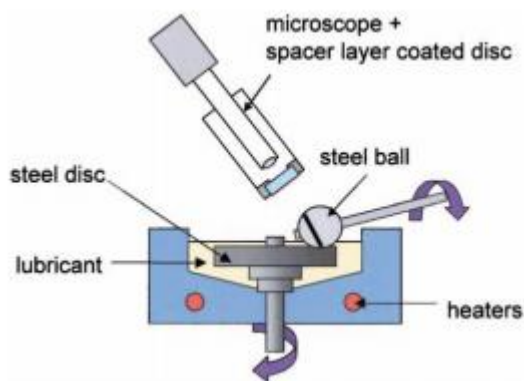


Figure 1. Diagram of MTM-SLIM set up [7] 33

34

35 The tribological tests were split into three alternative stages which were carried out at fixed
36 time intervals, with an overall two hour testing period. The first stage, known as the
37 conditioning phase, included rubbing the ball and disc together at a fixed slow entrainment
38 speed in the mixed lubrication regime to encourage the formation of tribofilm on the ball and
39 disc wear track. This was then followed by applying the Stribeck curve parameters, starting

1 at a high speed - 2 m/s (mixed regime) and continued towards the lowest speed value - 0.01
 2 m/s (boundary regime). The final stage involved halting the test and the ball sample was
 3 loaded against the spacer layer-coated window, where an image was captured which would
 4 allow the measurement of the tribofilm. *Table 1* summarises the conditions used with the
 5 tribometer within this study.

6

7 **Table 1. Test conditions used with MTM2 - SLIM**

Conditioning Phase	
Temperature	80°C
Load / Hertzian Contact Pressure	36 N / 1 GPa
Entrainment Speed	0.1 m/s
Sliding-rolling Ratio	150%
Stribeck Curve Phase	
Temperature	80°C
Load / Hertzian Contact Pressure	36 N / 1 GPa
Entrainment Speed	2 to 0.01 m/s
Sliding-rolling Ratio	150%

8

9 **2.2 Materials and lubricants**

10 The material used for this investigation is nitriding steel, generally used for components
 11 subjected to high friction and wear. The ball shaped samples had a hardness of ~300HV₁ prior
 12 to treatment. To carry out the oxy-nitriding heat (QPQ) treatment on the samples, it involved
 13 using a cyanide/cyanate bath at 400-600°C to form a ~19 µm nitride layer (Fe₂₋₃N & Fe₄N),
 14 followed by using a specialised nitrate – nitrite cooling salt bath to form a 0.5 µm oxide layer
 15 (Fe₃O₄) on top, which acts as a protective running-in coating (800-830 HV₁) – the process is
 16 highlighted in *Figure 2* [12]. Polishing and finishing are used to achieve a smooth surface
 17 finish - R_a – 30 nm.

18

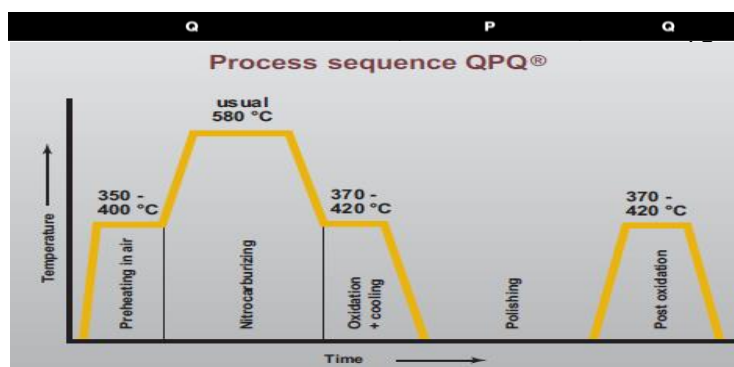


Figure 2. Salt bath nitriding (QPQ) heat treatment process [12].

26 The alternate treatment applied within this study involved using a gas-nitrided hardened ball
 27 sample, on which a 9 µm molybdenum disulphide (MoS₂) running-in coating was sprayed on
 28 top (750-780 HV₁). This coating is typically used in systems where lubricants are deemed

1 ineffective. After treatment the ball samples had a surface roughness – R_a – 680 nm. The key
2 processes to the application of the coatings are highlighted in *Figure 3* [13].

3 The spheroidal graphite cast iron counter discs were gas nitrided and this treatment was kept
4 constant for all counter surfaces, leaving the sample with a surface finish - R_a – 50 nm. The
5 wear on the plate samples post-experiments were negligible so surface analysis mainly
6 focussed on the treated ball samples.

7 The base oil (BO) used was a group I mineral oil with a viscosity of 5.2 cSt at 80°C. Lubricant
8 one and two were a mixture of BO and SO or TCP respectively (*Table 2*).

9 **Table 2. Lubricants tested**

1.	BO + SO (1.5%)
2.	BO + TCP (0.25%)

10

11

12

13

14

15

16

17

18

19

20

21

22

23

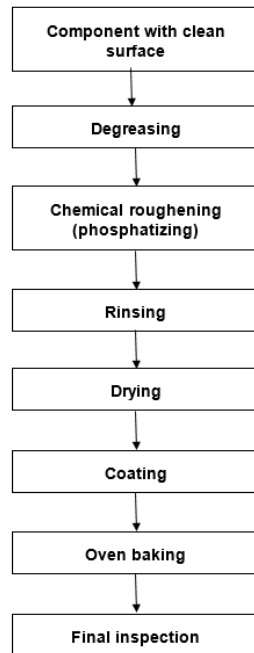


Figure 3. Schematic diagram for the application of the MoS_2 coatings [13].

24 2.3 Morphology and Topography Analysis

25 The changes in surface topography of the different samples were analysed using a Leica
26 optical microscope and a Taylor Hobson Talysurf Profilometer, which allows the
27 measurement of the depth of the wear scars formed on the ball samples.

28 2.4 Tribofilm Chemical Properties

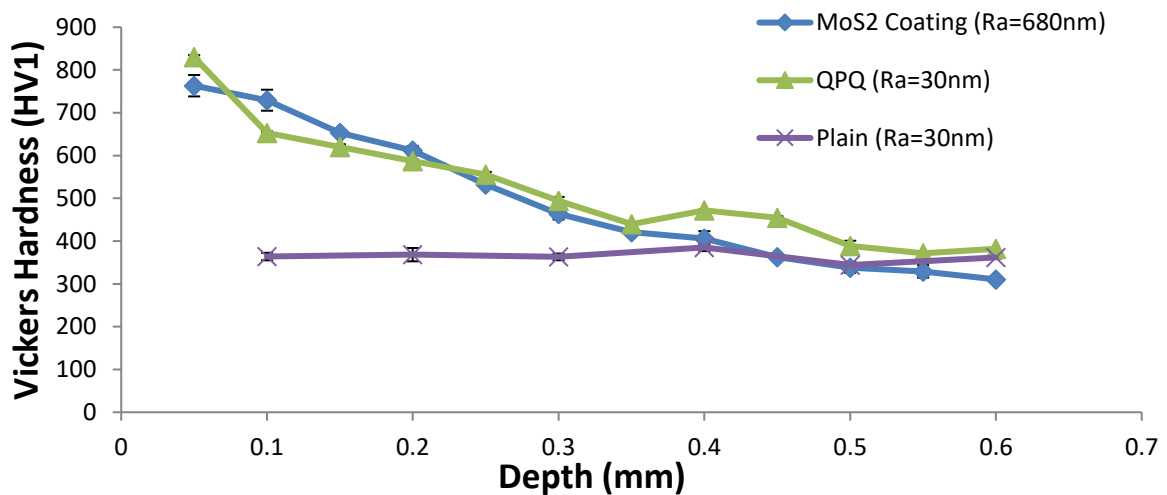
29 Post experimental surface analysis included carrying out X-ray Photoelectron Spectroscopy
30 (XPS) on the worn surfaces of the pin samples to identify the chemical species present in the
31 tribofilms formed which could essentially affect friction and wear. A monochromatized Al
32 $K\alpha$ X-ray source was used to carry out high resolution scans for specific peaks. The beam line
33 was focused in the centre of the wear scar in an area of $200 \mu\text{m} \times 200 \mu\text{m}$. The tribofilm was

1 also etched (0.2 min) and the charging effects in the results were corrected by fixing the C1s
2 peak (adventitious carbon) at 284.8 eV. Casa XPS software which applies a Shirley algorithm
3 to construct a background, through a curve fitting procedure, which is applied to the peaks
4 identified. To accurately determine the chemical species present the peak's area and full-width
5 at half-maximum (FWHM) were constrained.

6 3. Results

7 3.1 Surface Characterisation

8 Microhardness measurements have been carried out with Micro Vickers microhardness tester
9 using a load of 9.81 N (1 kg) across the samples cross-sections. The results are presented in
10 *Figure 4*. *Figures 5 & 6* show the SEM morphologies through the cross-section of each treated
11 samples (QPQ and MoS₂). The Taylor Hobson Form Talysurf was employed to measure the
12 surface roughness of the samples.



13

Figure 4. Comparison of the hardness through each of the treated samples cross-section and also their surface roughness.

14

15 The plain (untreated) samples were shown to mainly be composed of pearlite and ferrite
16 matrices. For the QPQ samples (*Figure 5*) three distinctive layers are detected; on the very
17 top surface a very thin black oxide layer of ~0.5 μm thickness is present. Underneath this
18 layer is a ~19 μm thick compound layer of a porous constitution. The final visible layer was
19 a diffusion zone of approximately ~250 μm thickness.

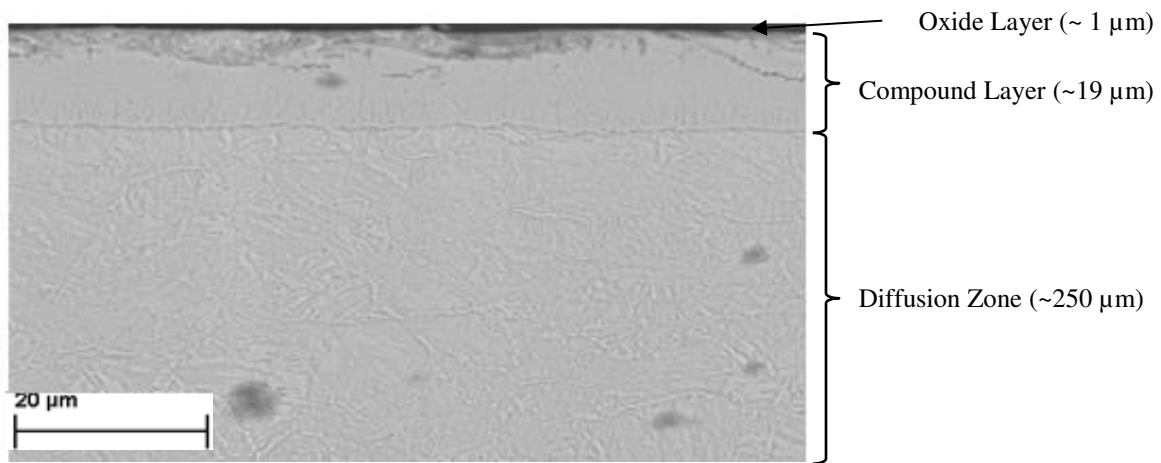
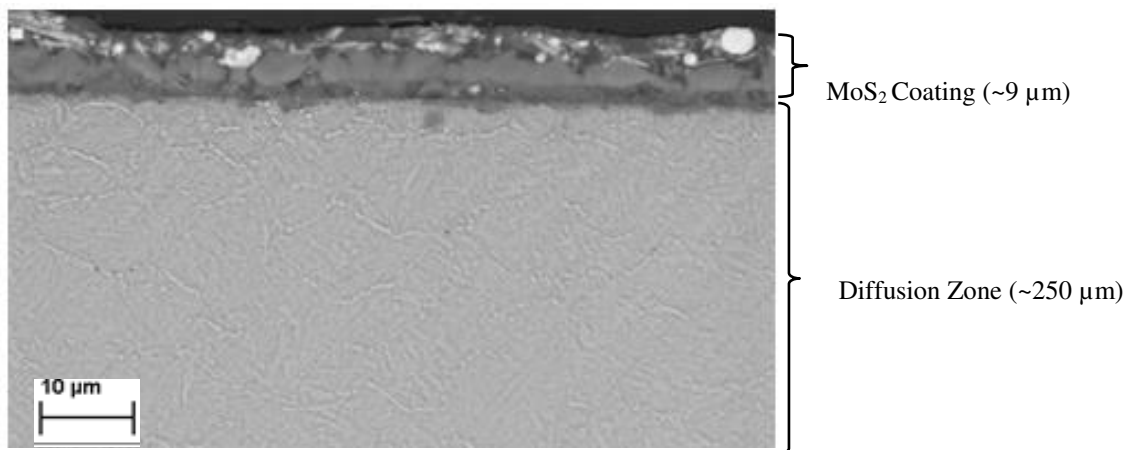


Figure 5. SEM image profile through the cross-section of a QPQ ball sample.

2



3

Figure 6. SEM image profile through the cross-section of a MoS₂ coated ball sample.

4

5

6 Compared to the QPQ samples, on the balls coated with MoS₂ (Figure 6) it is possible to see
 7 a thick layer (~9μm) followed by a diffusion zone formed by the original gas nitriding of the
 8 sample. The sample was originally hardened using the gas nitriding process before the formed
 9 nitride layer was removed, leaving the diffusion zone.

10 3.2 Tribofilm Formation from MTM SLIM Tests

11 Figures 7-20 show a series of Stribeck friction curves measured during a 2-hr rubbing test
 12 using BO+SO & BO+TCP. They highlight the dynamics of the different treated surfaces with
 13 the lubricant throughout the mixed and boundary lubrication regimes. On each graph the
 14 change from boundary (1-100 mm/s) to mixed lubrication (100-10000 mm/s) is highlighted
 15 by a dashed red line. These graphs are combined with a series of optical interference images
 16 of the tribofilms formed on the surface of the treated balls, which would be indicated by dark
 17 areas. The sliding direction in all these images is from left to right. Due to the roughness of
 18 the ball samples and in some cases the relative thinness of the formed tribofilm, it was not
 19 possible to quantify the film thickness accurately.

1 3.2.1 BO+SO - Friction & Wear

2 *Figure 7* shows the friction coefficient as a function of entrainment speed for the SO additive
3 with the QPQ treated sample. As the entrainment speed is reduced friction steadily increases.
4 In the mixed lubrication regime from 100 mm/s – 2000 mm/s, it is possible to see that friction
5 begins to reduce with time until the entrainment speed reduces below 100 mm/s (boundary
6 regime) where friction remains constant for the 2-hr rubbing period at the lower speeds. The
7 optical interference images (*Figure 8*) show virtually no tribofilm was formed during the
8 duration of the test. The optical interference images show that the wear of the sample
9 increased with time, shown by the distortion of the wear track in the SLIM image.

10 A different trend is observed with the MoS₂ coated sample (*Figure 9*), where at all entrainment
11 speeds with an increase in time the friction coefficient is seen to reduce steadily. The reduction
12 in friction after the two hour testing period at the different entrainment speeds ranged from
13 20-40%. The MoS₂ coated surface was significantly more sensitive to the SO additive than
14 the QPQ samples. The SLIM images (*Figure 10*) showed the formation of a thin tribofilm and
15 the exposure of a rougher surface than that observed when using QPQ samples (*Table 2*).
16 Once again the wear of the sample increased with the duration of the test as shown by the
17 distortion of the wear track from the SLIM images.

18

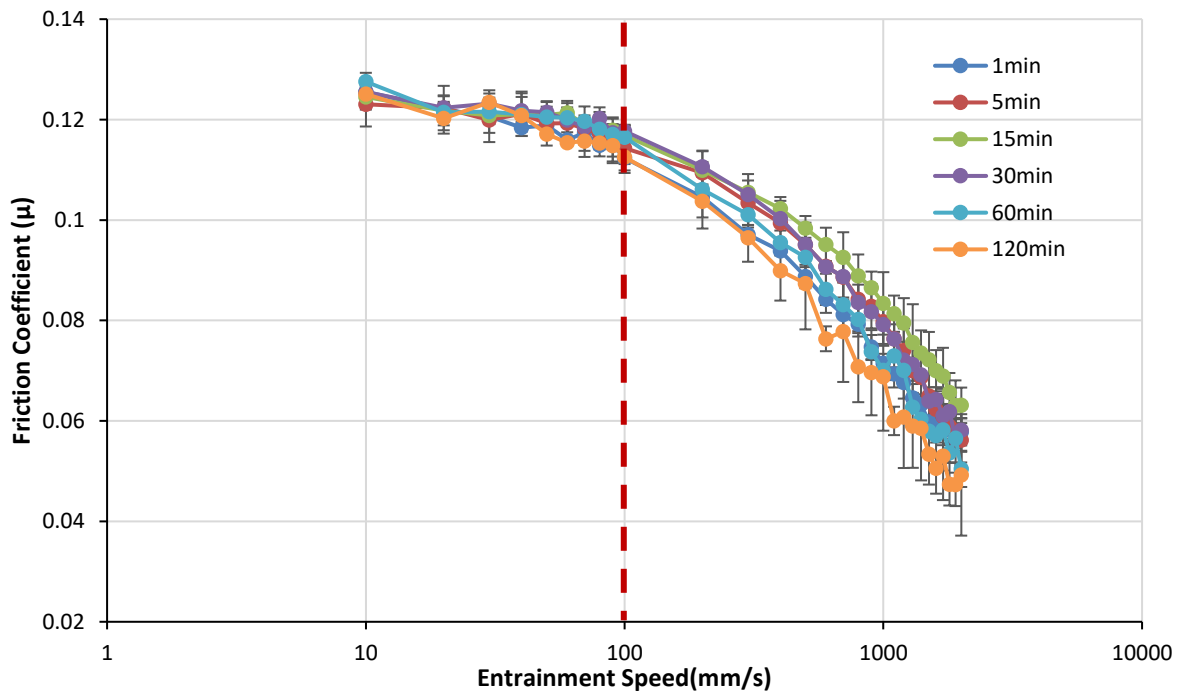


Figure 7. Series of Stribeck curves when using a QPQ ball and gas nitrided disc with BO+SO lubricant

19
20
21
22

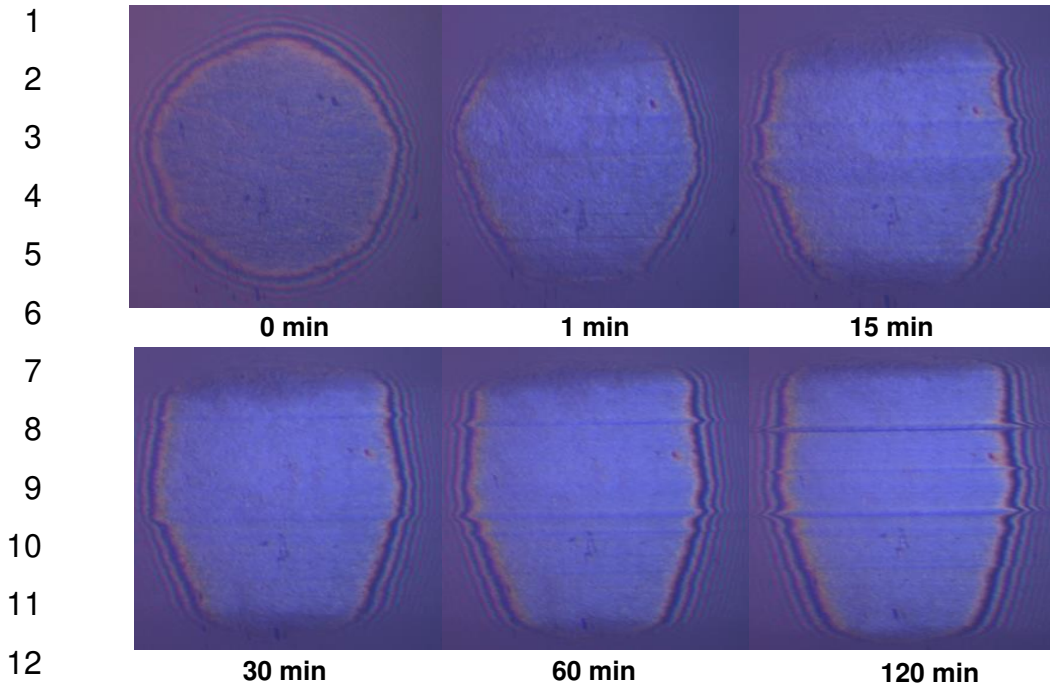


Figure 8. Optical interference (SLIM) images of the tribofilm formation on QPQ samples with BO+SO lubricant

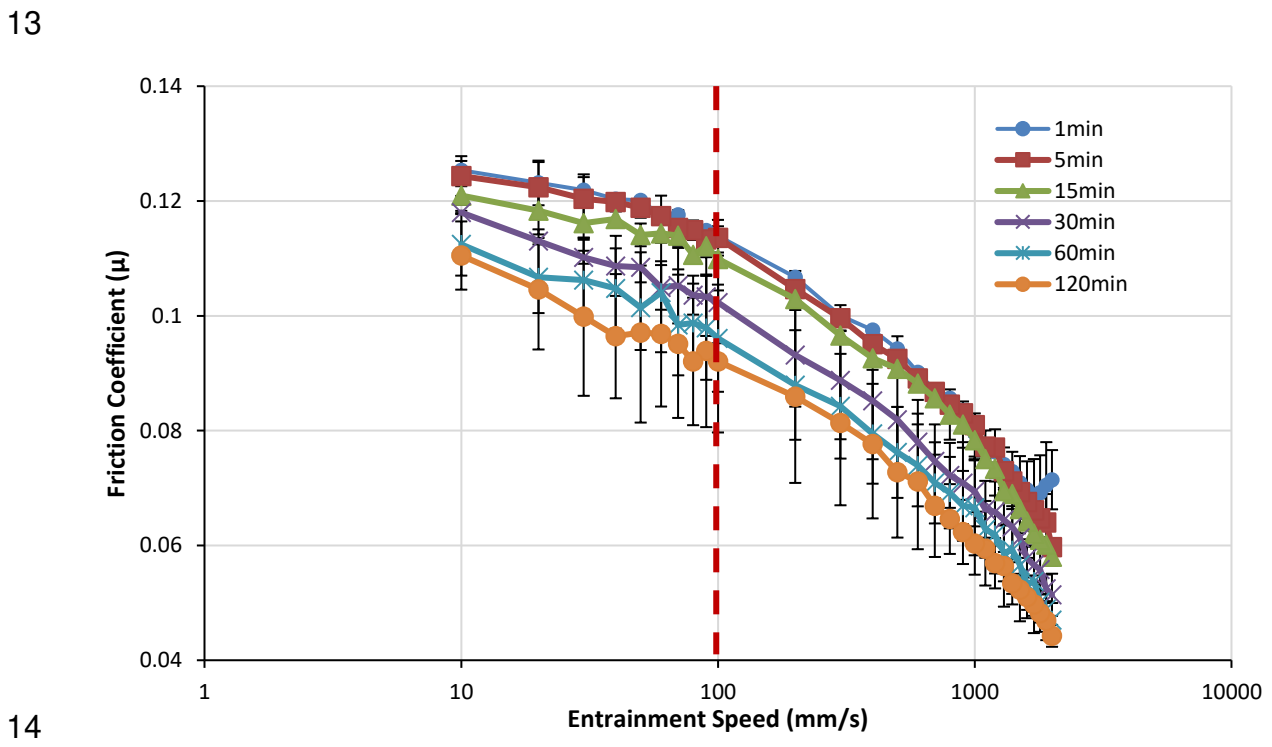


Figure 9. Series of Stribeck curves when using a MoS₂ coated ball and gas nitrided disc with BO+SO lubricant

15
16
17

1
2
3
4
5
6
7
8
9
10

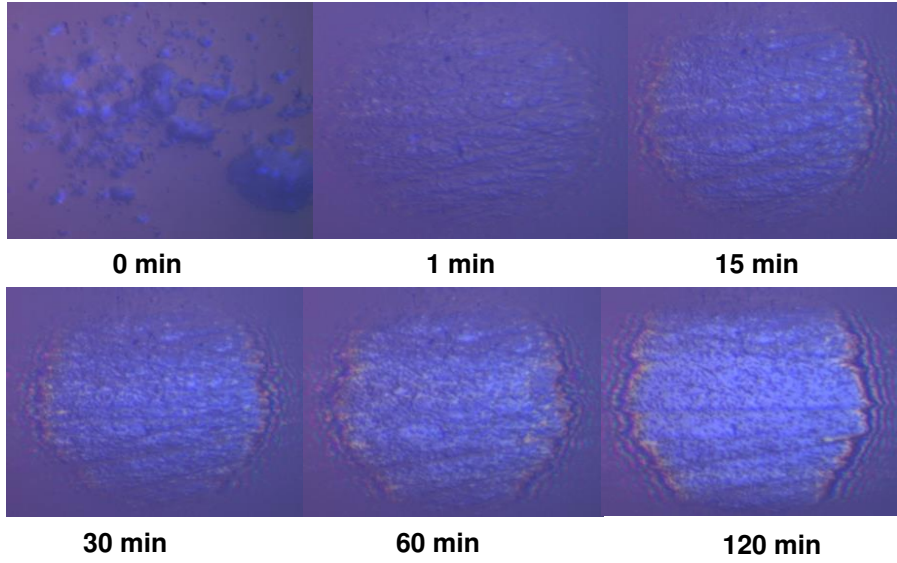


Figure 10. Optical interference (SLIM) images of the tribofilm formation on MoS₂ coated samples with BO+SO lubricant

11
12

Table 2. The roughness (R_a) of the treated ball samples pre and post testing when using the SO additive

	R _a (μm) Pre-test	R _a (μm) Post-test
QPQ Ball Sample	0.03	0.22
MoS ₂ Ball sample	0.68	1.71

13

14 When comparing the friction performance of the two treated samples, *Figure 11*, after 2hrs it
 15 is possible to see that the MoS₂ coated sample performed better in both boundary and mixed
 16 regime, producing lower friction values. The values at higher entrainment speeds merge;
 17 indicating that the nature of the surface at this point is having less effect than at lower
 18 entrainment speeds. The MoS₂ samples showed a higher variation in repeatability in
 19 comparison to the QPQ samples, however the lower friction trends are still evident.

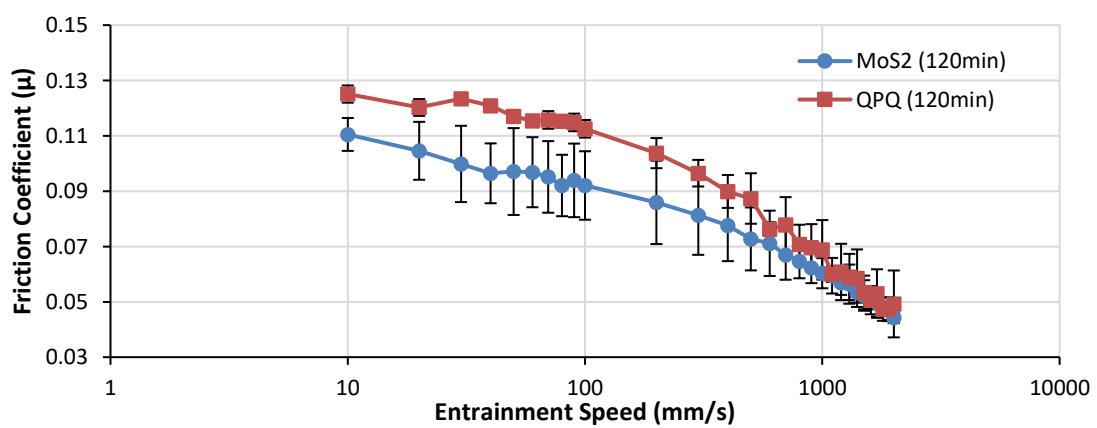


Figure 11. Comparison of the Stribeck curves after 2hr rubbing test for QPQ and MoS₂ coated samples and gas nitrided disc with BO+SO lubricant.

20

1

2 Optical images of the worn area of the QPQ MTM ball samples (Figure 12(a)) after testing
3 showed the removal of the oxide layer ($\sim 1 \mu\text{m}$) and the exposure of a porous compound
4 layer. There are signs of scoring across the surface. No clear tribofilm is identified on the
5 worn surface.

6 However with the MoS_2 ball samples (Figure 12(b)) the worn surface shows the almost
7 complete removal of the MoS_2 coating ($\sim 9 \mu\text{m}$), with only remnants of it being observed in
8 the wear scar. Scoring is observed across the surface alongside the presence of a uniform
9 tribofilm covering the worn area.

10 In terms of wear (Figure 13), the MoS_2 coated samples had greater wear depths and
11 penetration than the QPQ samples. The wear scar images and depth analysis indicate the MoS_2
12 coating was removed during testing.

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

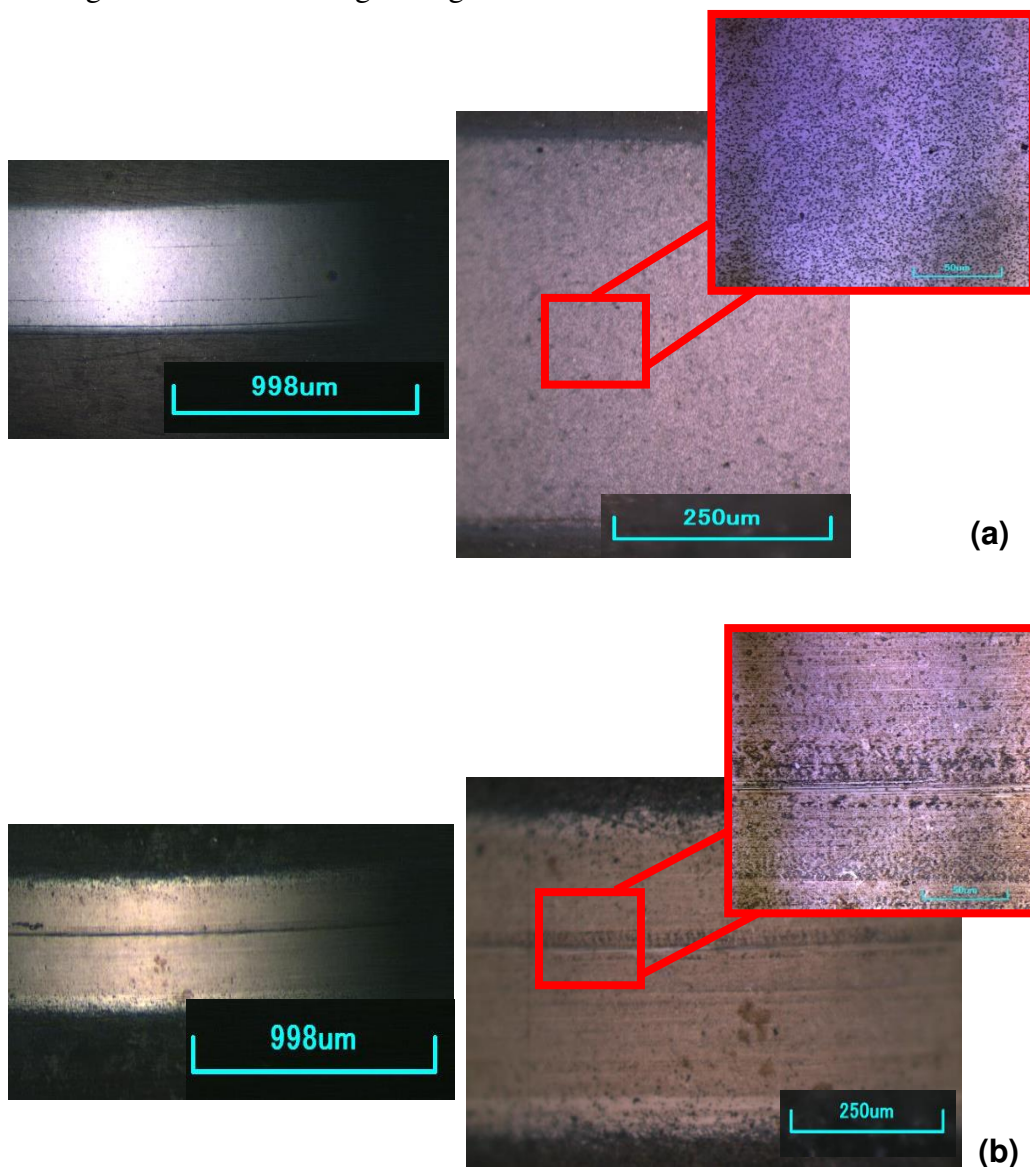


Figure 12. Optical images of wear scar regions of the MTM ball samples with the SO additive – (a) QPQ ball (b) MoS_2 ball.

1

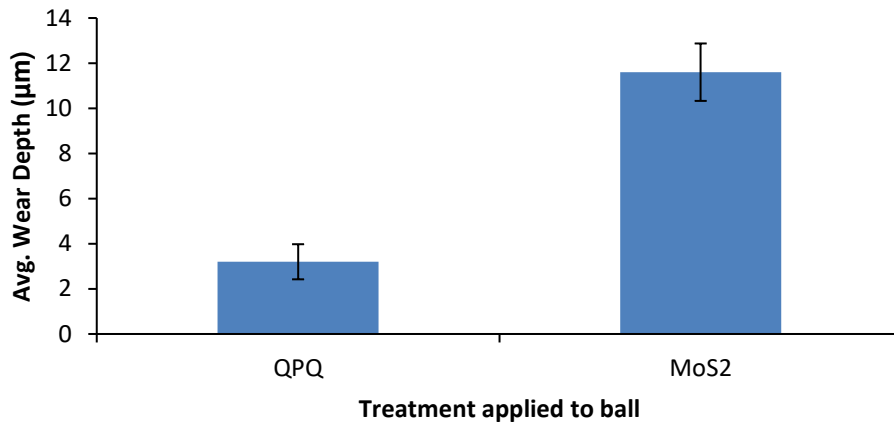


Figure 13. Comparison of the wear depths of QPQ & MoS₂ coated ball samples when using BO+SO.

9 3.2.3 BO+TCP - Friction & Wear

10 *Figure 14* shows the friction coefficient of TCP additive with the QPQ treated sample. As the
11 entrainment speed is reduced friction steadily increases. In boundary condition it is possible
12 to see that friction is constant throughout the two hours of the test. In the mixed regime friction
13 begins to reduce slightly with time. However taking into consideration statistical error the
14 change does not seem significant. The SLIM images are similar to those from the SO oil tests
15 and no clear tribofilm is formed. However at 60 and 120 minutes a thin tribofilm seems to be
16 present as highlighted in *Figure 15*. The SLIM images show less distortion of the samples
17 wear track with time compared to using the SO additive, suggesting lower wear is occurring.

18 With the MoS₂ coated sample, in boundary regime there seems to be no change in friction
19 during the duration of the two hour test (*Figure 16*), there is a slight reduction in friction
20 within the mixed regime with time however the behaviour is similar to that seen with the QPQ
21 sample and the change is not significant. The optical interference images show the formation
22 of a tribofilm on the wear track (*Figure 17*), composed of non-uniformly distributed patches
23 elongated along the sliding direction developing in thickness with the duration of the test. The
24 images also show the shape of the wear track is maintained during the test. The wear scar
25 shows signs of adhesive wear and the surface is once again rougher than using the QPQ
26 sample (*Table 3*).

27 Even with the formation of a tribofilm on both sample variants there was no real impact on
28 friction. This indicated that the properties of the tribofilm formed when using the TCP additive
29 were different to that observed when using the ZDDP additive which lead to an increase in
30 friction as observed by Yue *et al* [6].

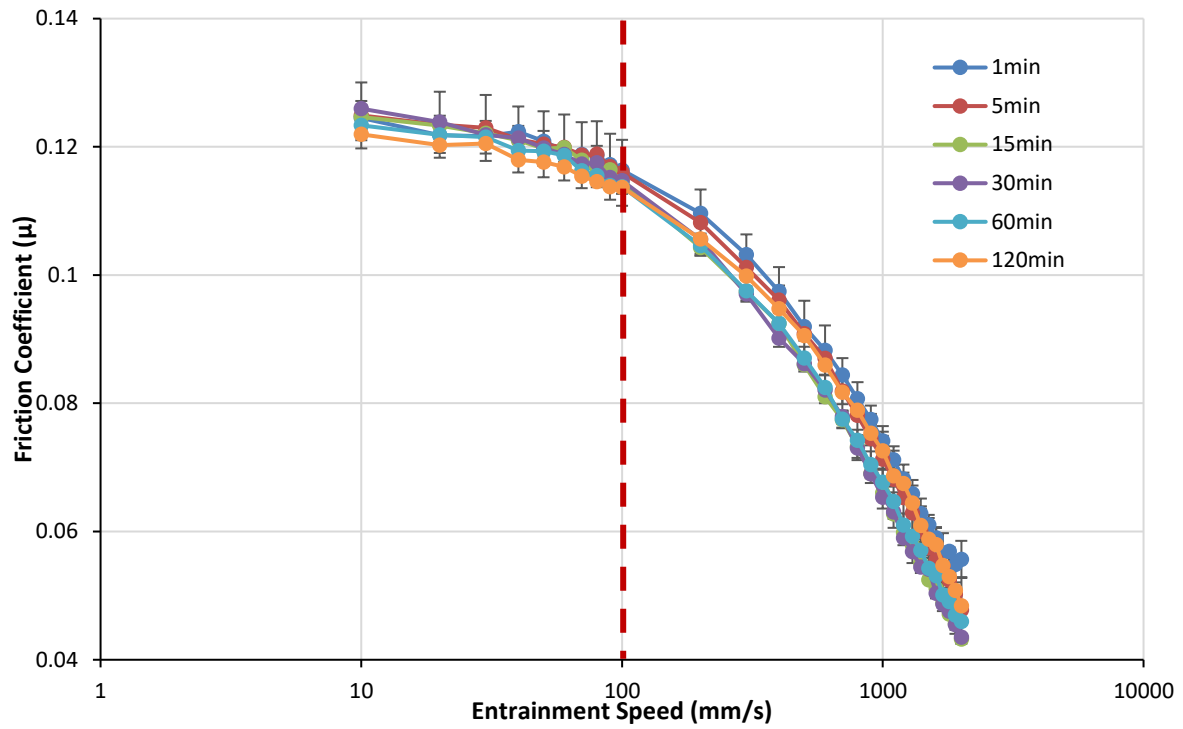


Figure 14. Series of Stribeck curves when using a QPQ ball and gas nitrided disc with BO+TCP lubricant.

1
2
3
4
5
6
7
8
9
10
11
12
13
14

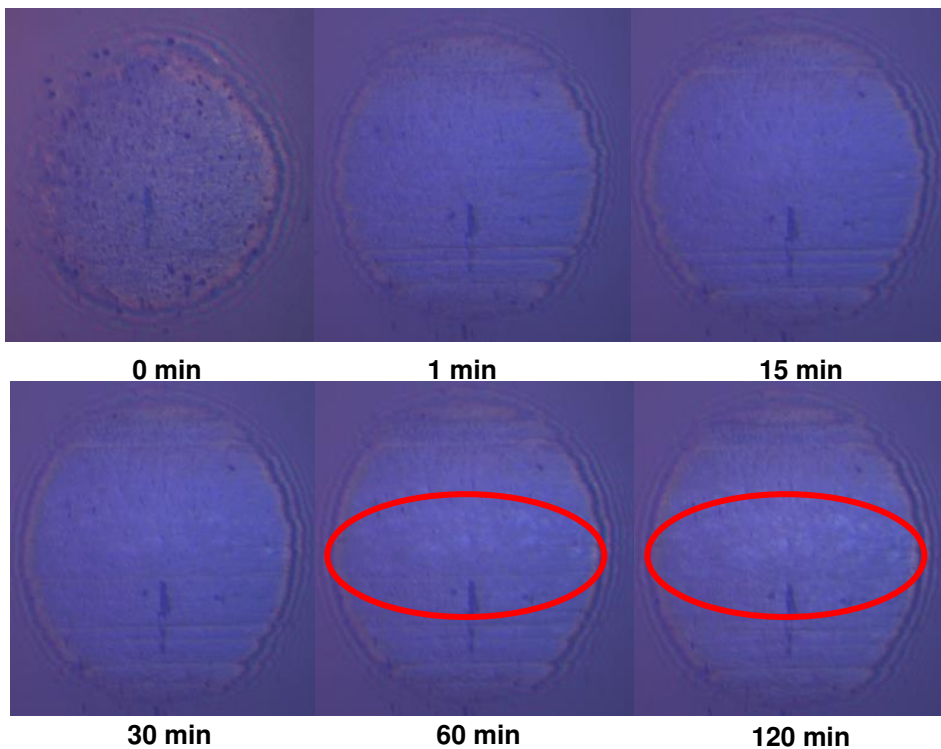


Figure 15. Optical interference (SLIM) images of the tribofilm formation on QPQ samples with BO+TCP lubricant

15

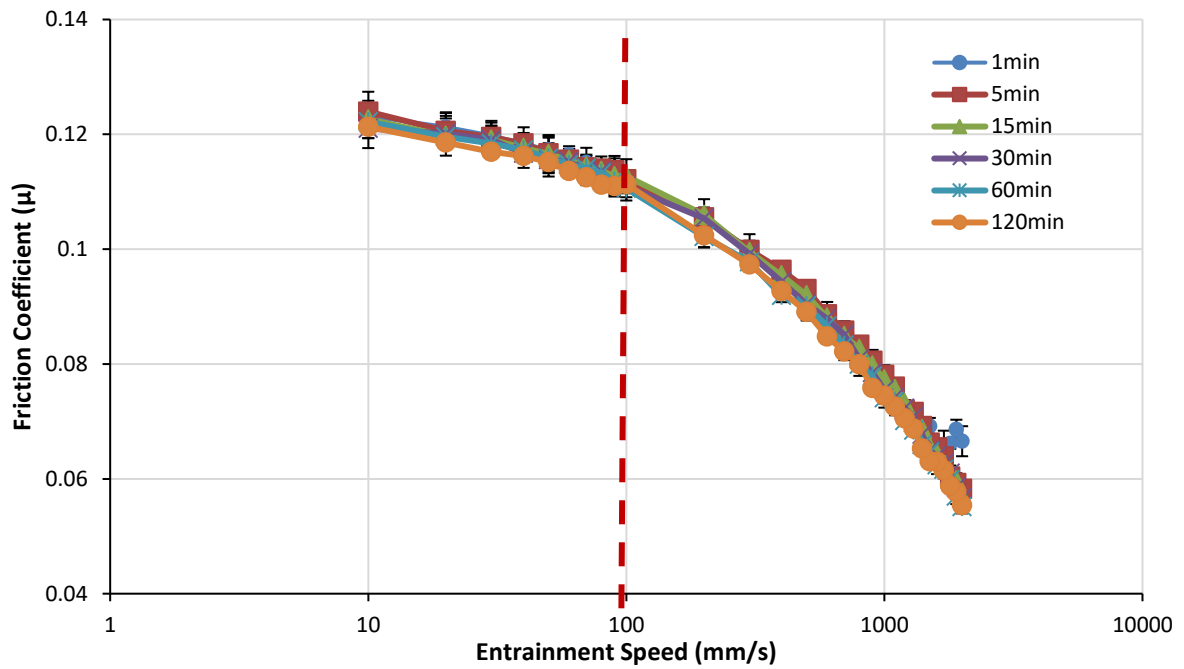


Figure 16. Series of Stribeck curves when using a MoS₂ coated ball and gas nitrided discs with BO+TCP lubricant.

1
2
3
4
5
6
7
8
9
10
11
12
13

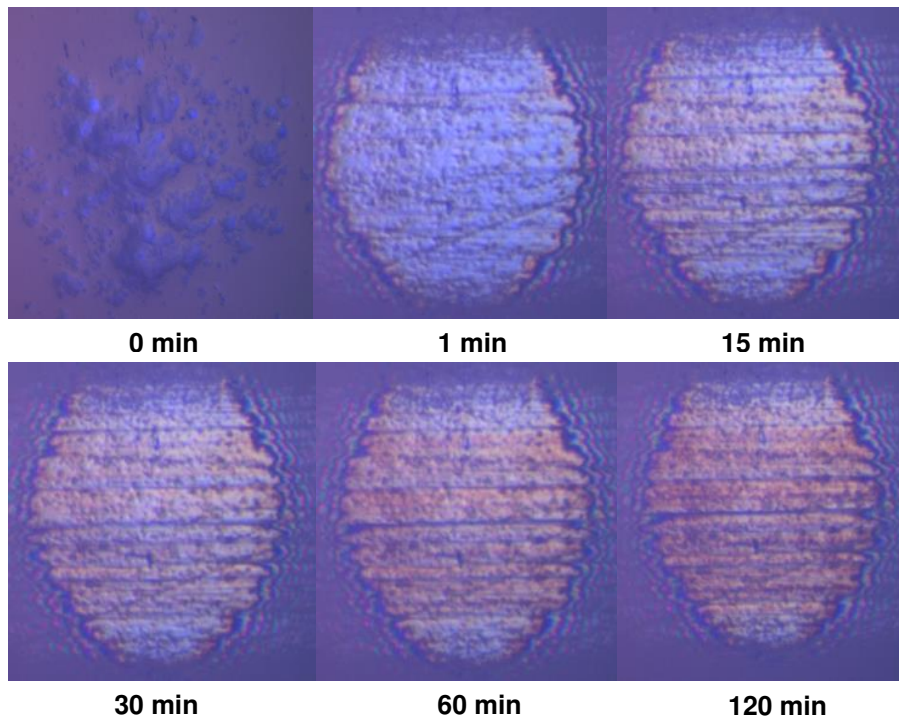


Figure 17. Optical interference (SLIM) images of the tribofilm formation on MoS₂ coated samples with BO+TCP lubricant

14

1 **Table 3. The roughness (R_a) of the treated ball samples pre and post testing when using the TCP**
 2 **additive**

	R_a (μm) Pre-test	R_a (μm) Post-test
QPQ Ball Sample	0.03	0.14
MoS₂ Ball sample	0.68	1.35

3

4 When comparing the friction performance of the two treated samples, *Figure 18*, after 2hrs it
 5 seems the friction response of the two treated samples are almost identical.

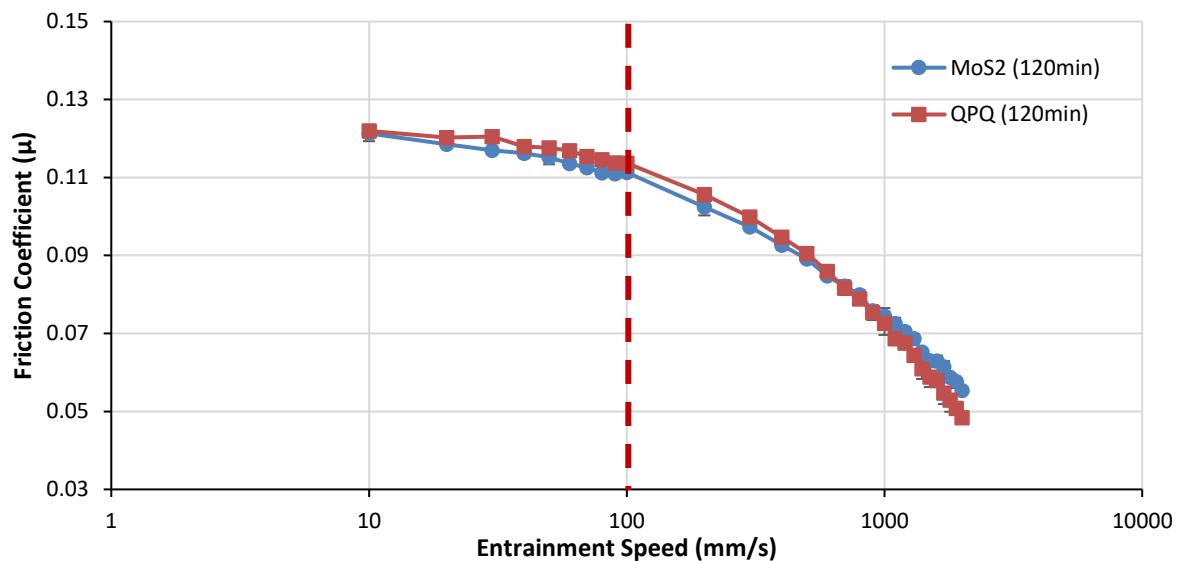


Figure 18. Comparison of the Stribeck curves after 2hr rubbing test for QPQ and MoS₂ coated samples gas nitrided discs with BO+TCP lubricant.

6

7 The wear track of the QPQ MTM balls (Figure 19(a)) with the TCP additive showed the
 8 partial wearing of the Fe₃O₄ oxide layer in contrast to using the SO additive (Figure 12(a)),
 9 where the layer was completely removed. Even though the Fe₃O₄ layer survived the test,
 10 sections of it were worn through. When using the TCP additive the presence of a tribofilm
 11 can be observed on the worn surface which was not the case when using the SO additive.

12 Similar to when using the SO additive, the MoS₂ coating was worn away with the TCP
 13 additive (Figure 19(b)) with only remnants present within the contact. A thicker tribofilm is
 14 observed to form on the surface.

15 However in terms of wear, once again the MoS₂ coated samples had greater wear depths than
 16 the QPQ samples (Figure 20). The wear analysis of the QPQ samples indicated wear was less
 17 than 1 μm , suggesting the oxide layer survived testing as supported by the optical images
 18 (Figure 12(a)). With the MoS₂ samples wear depths were similar to the thickness of the
 19 coating, which may explain the presence of remnants of the MoS₂ coating as observed by the
 20 optical images (Figure 19(b)).

21

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

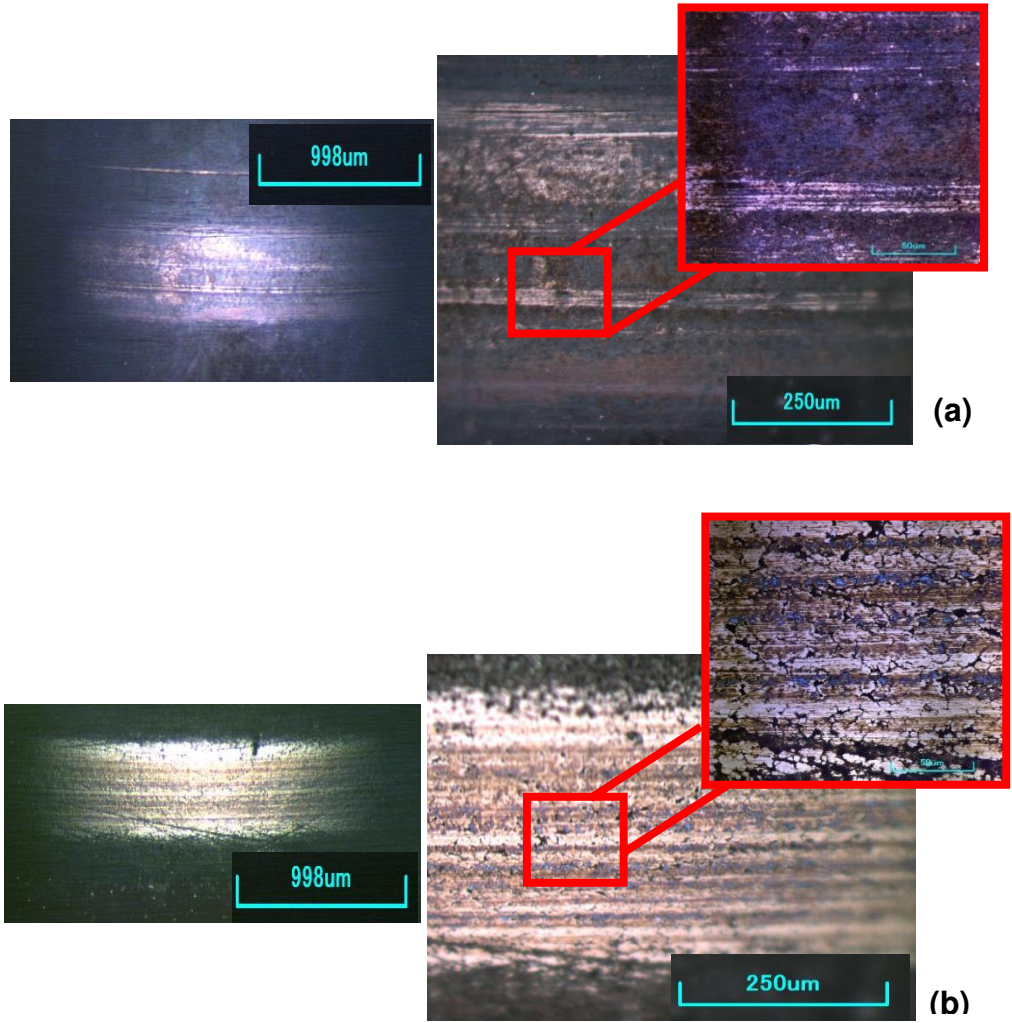


Figure 19. Optical images of wear scar regions of the MTM ball samples with the TCP additive – (a) QPQ ball (b) MoS₂ ball.

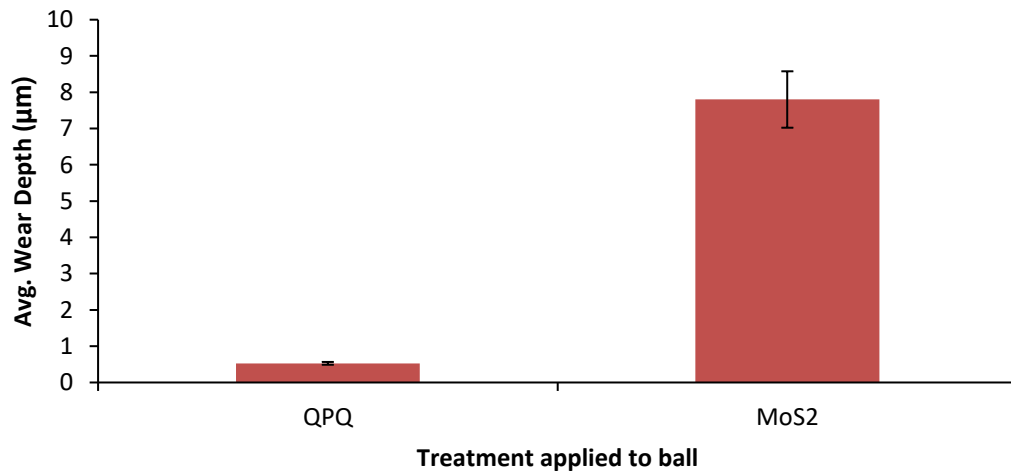


Figure 20. Comparison of the wear depths of QPQ & MoS₂ coated ball samples when using BO+TCP.

28
29

1 3.2.3 Effect of additives on treated samples

2 Using *Figure 21* to compare the friction response of the two additives with the QPQ samples,
 3 it is possible to see the friction trends are almost identical and the differing additives have no
 4 real affect when compared to each other. There is a stark comparison when analysing the
 5 effect of the different additives on the wear loss of the sample (*Figure 22*), the wear depth
 6 when using the TCP additive is significantly smaller than using the SO additive. The figure
 7 also shows that with both additives the wear never penetrated past the compound layer and
 8 into the substrate. The SLIM also showed the formation of a thin tribofilm with the TCP
 9 additive (*Figure 15*) whereas nothing was formed when SO (*Figure 8*) was used.

10

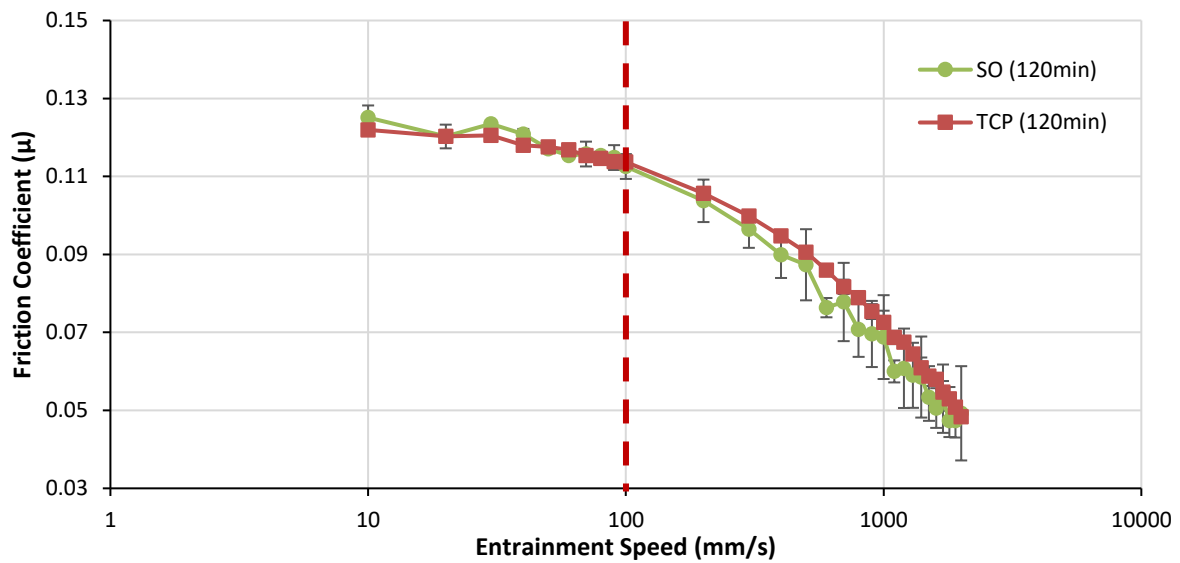


Figure 21. Comparison of the Stribeck curves after 2hr rubbing test for QPQ samples with gas nitrided discs when using BO+SO & BO+TCP lubricants.

11

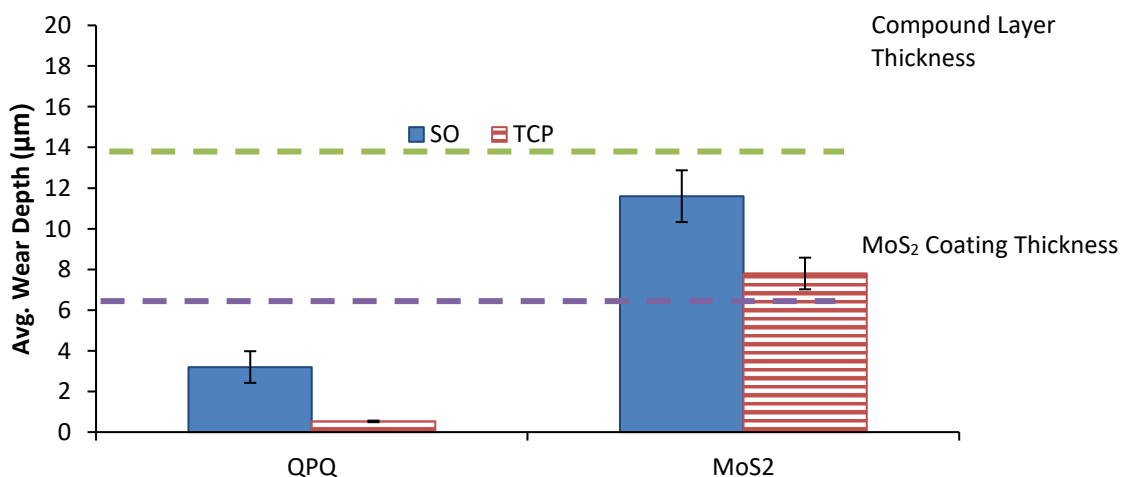


Figure 22. Comparison of the wear depths of QPQ & MoS₂ coated ball samples when using BO+SO & BO+TCP lubricants.

1 Analysing the effect of the different additives with the MoS₂ coated sample using *Figure 23*,
 2 the SO additive has a clear and effective impact on friction compared to the TCP additive.
 3 The SO additive produces significantly lower friction results in mixed and boundary
 4 conditions. However there is a different trend observed when comparing the depth of the wear
 5 scars on the ball, where the trend follows that seen with the QPQ sample. The samples tested
 6 with the TCP additives have smaller wear penetration (*Figure 22*), but for both oils it seems
 7 the coating did not survive the tests with the wear depth penetrating past the applied coating
 8 and into the substrate material. This is most likely due to the relative softness of the MoS₂
 9 coating. It had also been observed that a clear thicker tribofilm was formed when using the
 10 TCP additive, whereas it was thinner when using the SO additive.

11

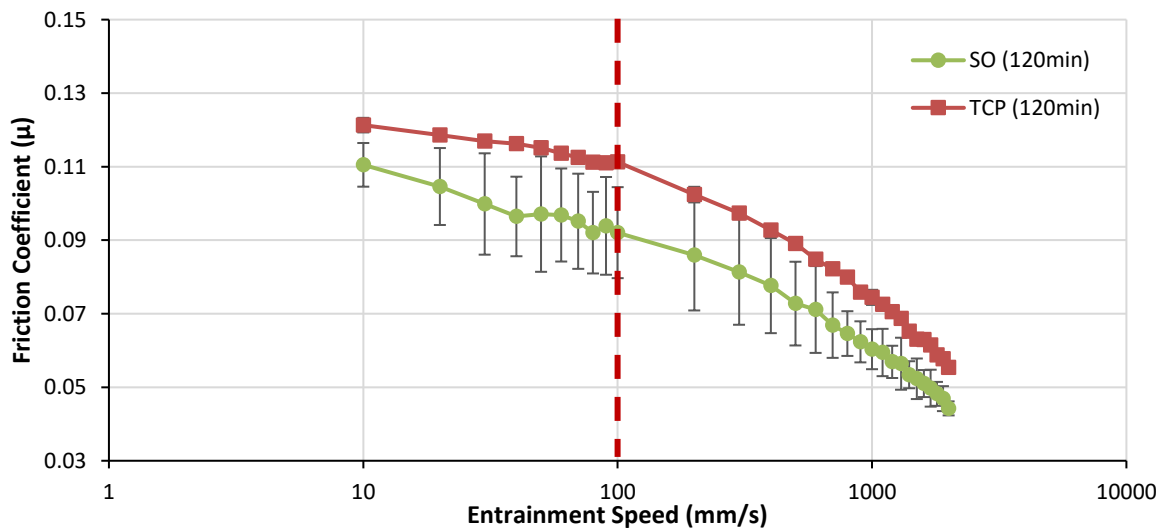


Figure 23. Comparison of the Stribeck curves after 2hr rubbing test for MoS₂ coated samples and gas nitrided discs when using BO+SO & BO+TCP lubricants.

12 3.3 XPS analysis on worn surfaces of MTM balls

13 XPS analysis was carried out to analyse the changes in chemical species formed in the
 14 tribofilms on the surface of the oxy-nitrided (QPQ) & MoS₂ coated samples when using the
 15 two different lubricant additives, which vary in elemental composition. *Table 4* and *Figures*
 16 *24-27* highlight the key species formed on the worn surface of the two sample types when
 17 using different additives. *Table 4* shows the species present at a 1.33 nm etching depth,
 18 alongside confirming the presence of a tribofilm with all the additives in this study. The XPS
 19 peaks show a higher intensity sulphur and phosphorous presence within the MoS₂ coated
 20 sample indicating a thicker layer has been formed. When using the SO additive with QPQ
 21 samples (*Figure 24*), there is a formation of FeS (~712.1 eV) and iron oxides. However when
 22 using the TCP additive (*Figure 26*) the key species identified are FePO₄ (~712.4 eV) and iron
 23 oxides. The same species formations were observed when using the MoS₂ coated samples
 24 (*Figures 25 & 27*), however when using the SO additive no traces of MoS₂ from the coating
 25 were detected in the wear scar. With the QPQ samples organic nitrogen species (~399 eV)
 26 were detected, which can be attributed to absorbed nitride complex [13].

1
2
3

Table 4. General binding energy values for compounds relevant to the tribofilms formed on the worn surface of the QPQ and MoS₂ samples when using the different EP additives at 0.2min etching time.

Sample Type	Additive	Element	B.E / eV (±1eV)	Chemical state
QPQ	SO	N 1s	399.0	Organic Species
		S 2p	162.3	Sulphide
		Fe 2p	712.1	FeS
	TCP	709.5	Fe ₃ O ₄	
		N 1s	398.1	Organic Species
		P 2p	133.4	Phosphate
MoS ₂ coating	SO	Fe 2p	712.4	FePO ₄
		709.3	Fe ₃ O ₄	
		S 2p	161.9	Sulphide
	TCP	Fe 2p	711.9	FeS
		709.0	Fe ₂ O ₃	
		P 2p	133.7	Phosphate
Fe 2p	712.4	FePO ₄		
710.3	Fe ₂ O ₃			

4

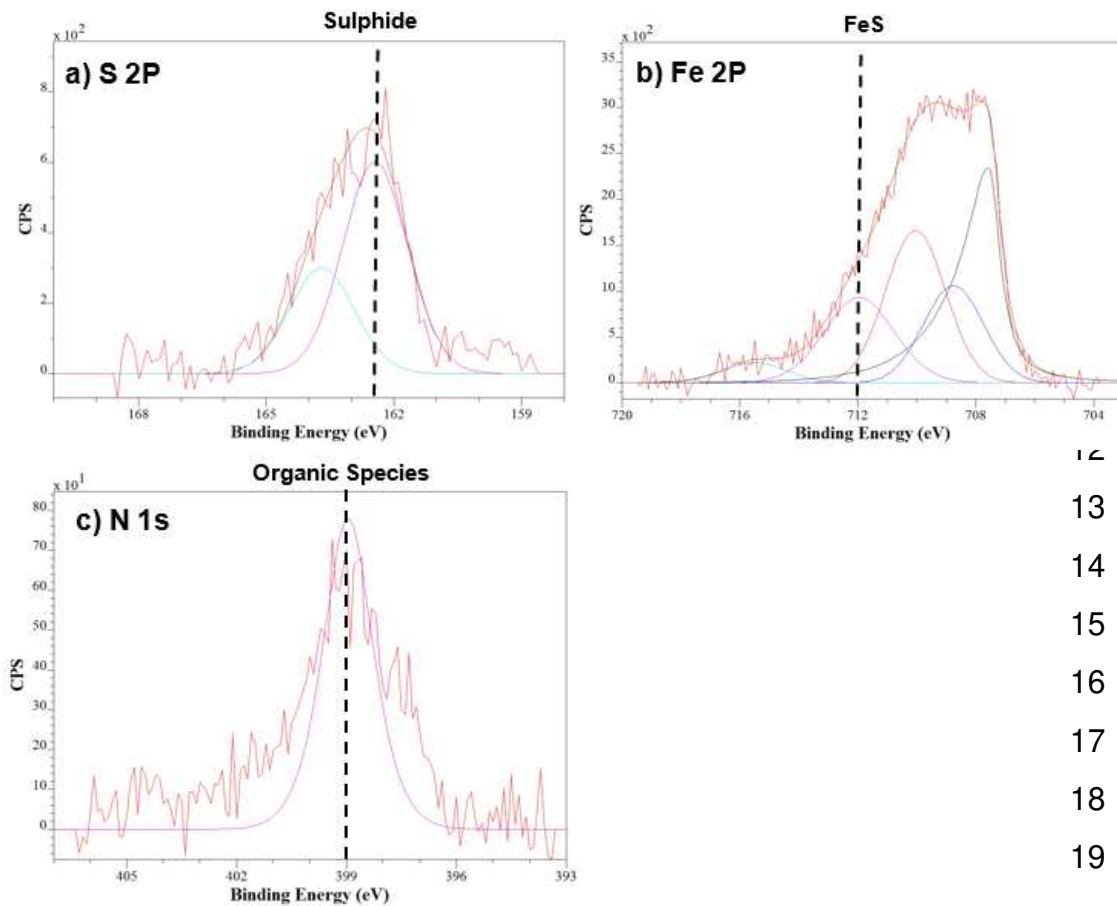


Figure 24. XPS spectra of S 2p, Fe 2p & N 1s on worn surface of the QPQ MTM ball samples at 1.33 nm etching depth with SO additive.

20

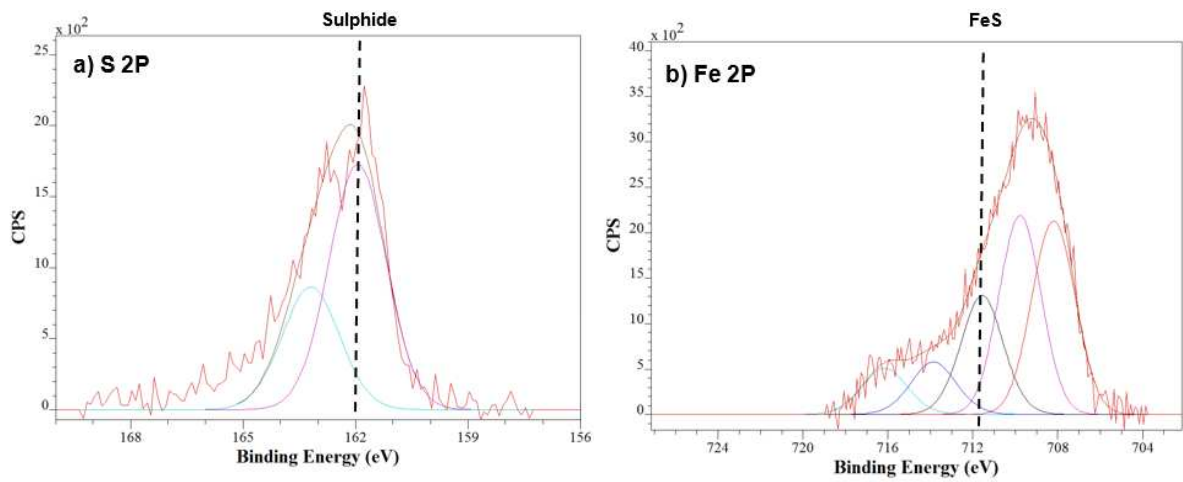


Figure 25. XPS spectra of S 2p & Fe 2p on worn surface of the MoS₂ coated MTM ball samples at 1.33 nm etching depth with SO additive.

1

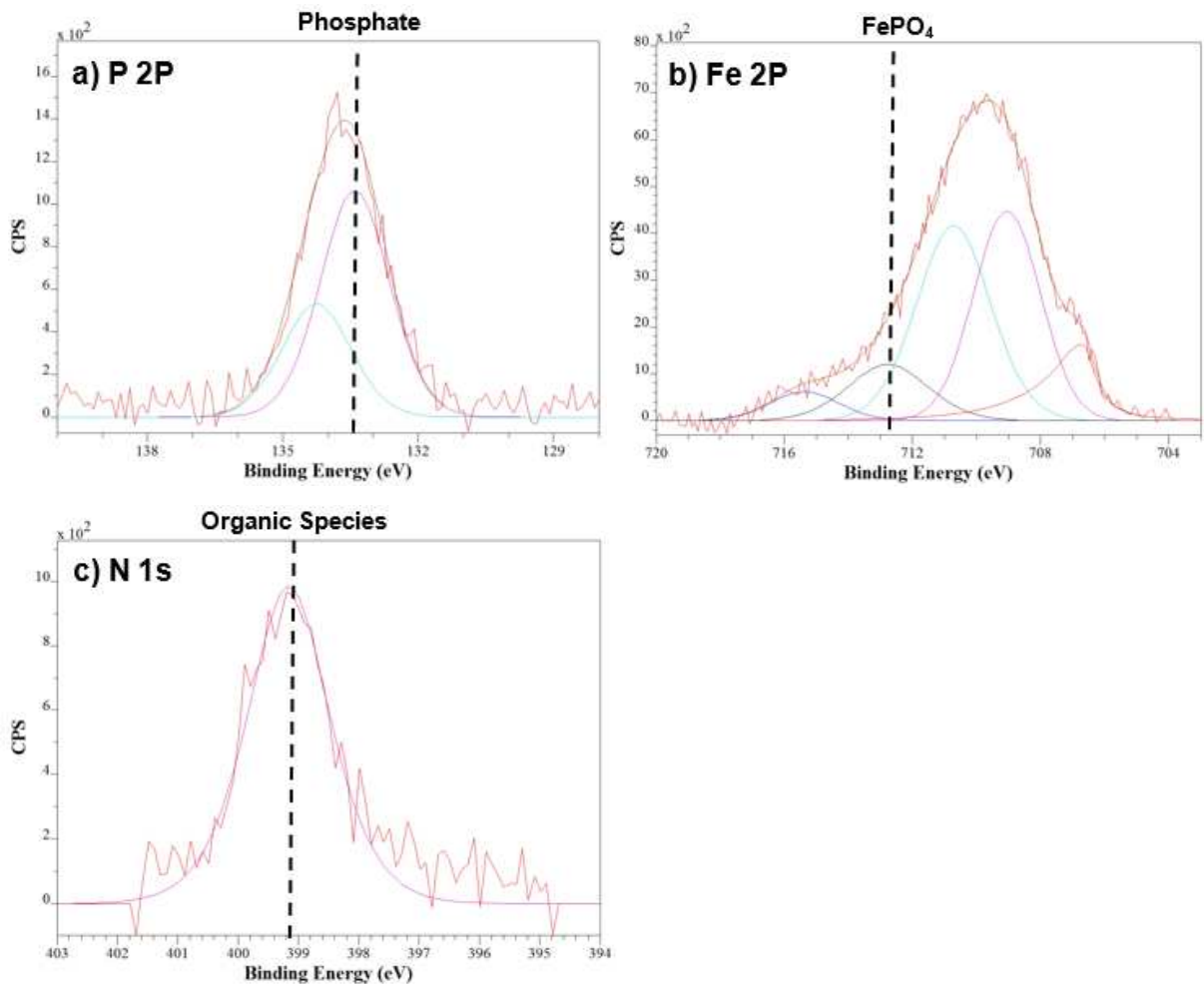


Figure 26. XPS spectra of P 2p, Fe 2p & N 1s on worn surface of the QPQ MTM ball samples at 1.33 nm etching depth with TCP additive.

2

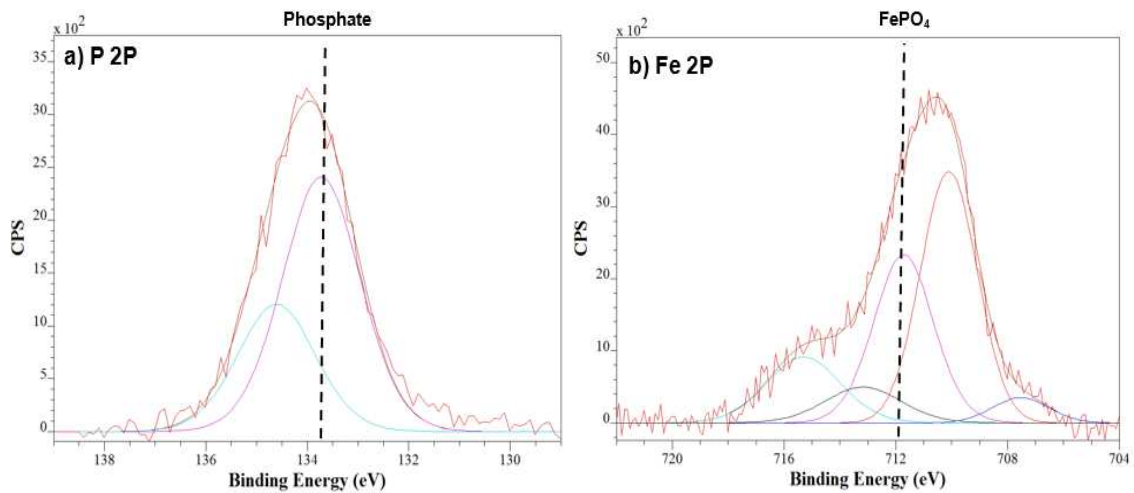


Figure 27. XPS spectra of P 2p & Fe 2p on worn surface of the MoS₂ MTM ball samples at 1.33 nm etching depth with TCP additive.

1

2 4. Discussion

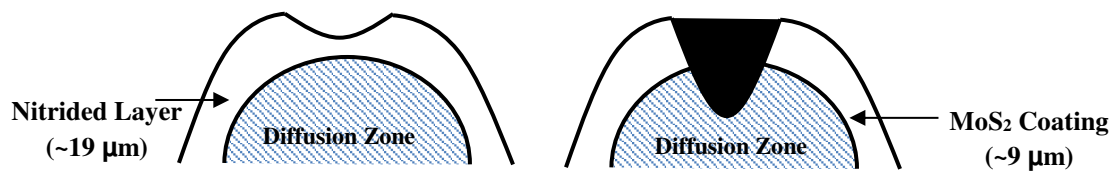
3 The tribological behaviour observed with the different treated samples is due to a combination
 4 of factors such as the mechanical properties and surface characteristics alongside
 5 tribochemical interactions with the lubricants used.

6 4.1 Friction and Wear

7 A common trend observed with the QPQ and MoS₂ treated samples with both additives was
 8 the reduction of friction with time. This may be due to a number of factors such as the removal
 9 of asperities of the ball's surfaces, which would allow greater entrainment of lubricant
 10 between two surfaces and hence a reduction in friction is observed with time or the drop in
 11 contact pressure due to the wearing of contacting surfaces. In some cases friction within
 12 boundary regime remained constant over time with both samples and additives; this may be
 13 due to the inability to form effective friction reducing tribofilm.

14 The wear depths of the MoS₂ coated samples were significantly higher than the QPQ balls,
 15 with the diffusion zone being exposed in all experiments (*Figure 28*). Bonded coating
 16 manufacturer Kluber [14] states that MoS₂ coatings are usually used as a running-in coating,
 17 with the durability of the coating being relatively short and once it has been worn through it
 18 cannot be replenished. The exposure of the diffusion zone suggests the coating is easily
 19 removed during testing and is of a softer nature, compared to the layers produced by nitriding.
 20 The properties of nitrided layers produced play a significant role in the tribological
 21 performance observed. Qiang *et al* [15] reported that the formation of a ϵ -phase composed
 22 compound layer with inter-metallic/ceramic properties makes it difficult for metallic
 23 counterparts to adhere with. This combined with a lamellar close packed hexagonal
 24 microstructure, which is easy to slide and to run in along the base plane would help to reduce
 25 the heat produced by friction. With the MoS₂ coated sample the rougher metallic diffusion
 26 zone surface (Tables 2 & 3) is exposed when using both additives, allowing it to adhere with
 27 the nitrided counter face in comparison to the QPQ sample where its ceramic layer interacts
 28 with that of the counter disc. The metallic surface interaction of the MoS₂ sample and counter

1 disc led to adhesive wear occurring at the contact surface, which was not seen with the QPQ
2 samples.



8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

Figure 28. Cross-sectional scheme of treated MTM ball samples worn surfaces

9 The impact of the properties of the modified surfaces on tribological behaviour are highlighted
10 in *Figure 22* where the QPQ samples are shown to have greater wear resistance than the MoS₂
11 coated samples. The figure also importantly shows that not only can the surface impact
12 behaviour but so can its interaction with the additives in the lubricant, which is investigated
13 further in the next section.

4.2 Surface Tribochemistry

15 The interaction of the different additive-containing lubricants with the treated samples played
16 a significant role in the tribological behaviour observed. It can be difficult to form a tribofilm
17 on a treated surface in some cases due to the reduction in reactivity with the lubricant additives
18 compared to a steel surface [3]. SLIM images when using the QPQ samples (*Figures 8 & 14*)
19 show no tribofilm presence when using SO and a very thin formation when using the TCP
20 additive. The compound layer present on the QPQ samples is known for its inert/inter-metallic
21 properties [16, 17] and with the absence of nascent iron in this layer, it is not surprising that
22 no or a very thin tribofilm is formed.

23 Using XPS to etch the worn surface of the QPQ samples it was possible to confirm the
24 presence of a thin tribofilms and to characterize the formed protective layers. With the
25 presence of the SO additive FeS is seen to form within the tribofilm of the QPQ samples.
26 However due to the inert properties of the nitride layer this may have prevented the formation
27 of sufficient concentration of FeS to impact the friction response of the system.

28 When TCP was used, there is a slight formation of a visible tribofilm and using XPS FePO₄
29 was detected alongside phosphates which would improve the anti-wear behaviour of the
30 sample, with *Figure 22* showing lower wear penetration compared to using SO. Overall the
31 TCP additive had no impact on friction but only on wear behaviour. Ma *et al* [8] believed the
32 presence of a film formed when using a TCP additive would improve the samples anti-wear
33 and load carrying properties whereas when using SO only the load carrying ability would be
34 enhanced. Kawamura *et al* [18] states that the crystal structure of FeS compounds formed
35 when using the SO additive would substantially affect the samples wear properties, hence this
36 is possibly the reason for why high wear is observed compared to when using TCP with both
37 types of samples. Even though the reduced reactivity of the compound layer [16, 17] limits
38 the formation of a thick tribofilm, the type of additive present within the lubricant can still
39 greatly impact the friction and wear performance as observed.

1 The key difference between the QPQ and MoS₂ samples was the absence of a less reactive
 2 compound layer which was replaced with a MoS₂ layer with the latter sample. *Figure 22*
 3 shows that the applied MoS₂ coating is almost completely removed during testing with both
 4 lubricant variants and the nascent iron rich diffusion zone was exposed. This allowed the
 5 formation of tribofilms containing higher concentrations of key compounds which could
 6 impact the tribological behaviour. With MoS₂ coated samples and TCP additive combination
 7 a thick tribofilm is seen to form (*Figure 17*), however the friction response of both samples
 8 (MoS₂ & QPQ) with the TCP additive were identical (*Figure 18*), supporting the assumption
 9 that the additive has no impact on friction. Instead wear resistance is improved due to the
 10 formation of a thick compact boundary lubrication film composed of FePO₄.

11 Even though a thin tribofilm is formed when using the SO additive (*Figure 10*), the MoS₂
 12 coated sample demonstrated a significant friction reduction response even when compared to
 13 the QPQ sample. XPS showed the formation of FeS within the tribofilm formed, this
 14 combined with the remnants of the MoS₂ coating would greatly influence the friction
 15 behaviour of the sample. A similar response was observed within Wang *et al's* [19] work with
 16 MoS₂/FeS multilayer films under lubrication (*Figure 29*), where the friction decreased and
 17 was lower than steel with an FeS film. Wang *et al* [19] proposed this was due both compounds
 18 possessing a close packed hexagonal crystalline structure allowing easy slip along the close-
 19 packed plane. With the formation of FeS on the worn MoS₂ coated surface, this multilayer
 20 film would be subject to plastic deformation creating a plastic flow layer over the worn surface
 21 which help to reduce friction within the system. However the relative softness of both
 22 compounds would have a detrimental effect on the wear rate of the sample.

23 The interactions of the SO and TCP additives with the MoS₂ coated samples again show the
 24 interaction of additive with modified surface can greatly impact the tribological performance
 25 as observed when using the SO additive.

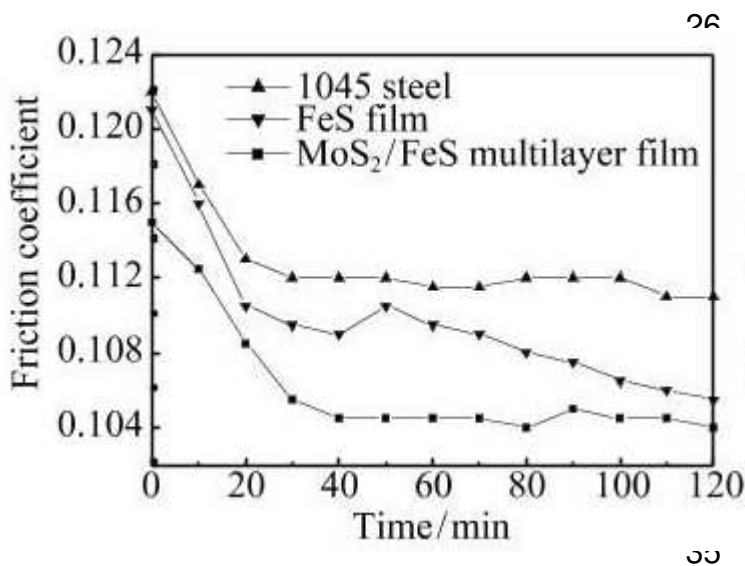


Figure 29. Friction behaviour of MoS₂/FeS multilayer, FeS film and steel under oil lubrication [19].

36 Ma *et al* [8] stated that the effectiveness of SO & TCP additives are determined by the
 37 presence of oxygen in the testing atmosphere. With the presence of an oxide layer on the QPQ
 38 sample surfaces it is assumed this would enhance the tribological performance of the samples.

1 When using the TCP additive significantly low wear was observed with the QPQ samples
2 (*Figure 22*), believed to be due to the interaction of the additive with the oxide layer. Guan *et*
3 *al* [20] believed that the mechanism of decomposition of TCP on an oxide layer involved a
4 chemical mechanism of decomposition with an initial P=O bonding of intact TCP to the
5 surface. This results in increased polarisation and activation of the P=O bond, followed by
6 nucleophilic attack of residual H₂O or surface O²⁻ onto the P-atom. Ultimately this results in
7 the formation of the metal phosphate or polyphosphate layer.

8 **5. Conclusions**

9 The effectiveness of extreme pressure and anti-wear additives on improving the friction and
10 wear characteristics of an oxy-nitrided and MoS₂ coated sample was investigated. This study
11 successfully highlighted that tribological performance can be influenced not only by the
12 properties of modified surfaces but also the lubricant additives used. The study allowed the
13 investigation of the interaction of sulphur and phosphorous containing additives with the
14 modified surfaces individually. The following was concluded:

- 15 (a) The properties of the layers produced after surface treatment can impact tribological
16 performance as seen with QPQ samples which showed lower wear penetration in
17 comparison to the alternative sample. The interaction of the surface with various
18 lubricant additives can further influence behaviour.
- 19 (b) XPS showed that when using the SO additive, FeS is formed, whereas with TCP
20 FePO₄ is detected to be present within the tribofilm. The presence of both compounds
21 could impact friction and wear behaviour.
- 22 (c) The SO & TCP additives respectively made minimal impact to modifying the friction
23 behaviour of the QPQ samples. The relative thinness of the FeS containing tribofilm
24 when using SO may have led to no impact on friction behaviour. The TCP also made
25 no change to friction reaction as expected but it significantly improved the anti-wear
26 and load carrying abilities of the surface.
- 27 (d) With TCP additive with the MoS₂ coated samples made no improvements to the
28 friction response of the sample however similarly to the QPQ sample there was a
29 drastic improvement to its anti-wear behaviour. When using the SO additive a
30 significant reduction in friction with time is observed due to the synergistic effect of
31 the FeS formed within the tribofilm and the MoS₂ coating.
- 32 (e) Even with the reduced reactivity of the QPQ sample the interaction of certain
33 additives can greatly impact the tribological performance of the surface.
- 34 (f) With MoS₂ coated samples with both additives the formation of a visible tribofilm is
35 observed however with QPQ samples there is not. This is most likely due to the
36 reduced reactivity of the compound layer of the QPQ sample preventing the
37 formation of a thicker tribofilm.

40 **Acknowledgements**

41 The authors would like to thank Komatsu Ltd and the University of Leeds for the funding of
42 this project and the supplying of test samples and oils.

1 6. References

- 2 [1] Manring, N.D., *Friction Forces Within the Cylinder Bores of Swash-Plate Type Axial-*
3 *Piston Pumps and Motors*. Journal of Dynamic Systems, Measurement, and Control, 1999.
4 **121**(3): p. 531-537.
- 5 [2] Nilsson, D. and B. Prakash, *Investigation into the seizure of hydraulic motors*. Tribology
6 International, 2010. **43**(1–2): p. 92-99.
- 7 [3] Yazawa, S., et al., *Reducing Friction and Wear of Tribological Systems through Hybrid*
8 *Tribofilm Consisting of Coating and Lubricants*. Lubricants, 2014. p.90-112.
- 9 [4] Wang, Y. and S.C. Tung, *Scuffing and wear behavior of aluminum piston skirt coatings*
10 *against aluminum cylinder bore*. Wear, 1999. **225–229**, Part **2**(0), p. 1100-1108.
- 11 [5] Neville, A., et al., *Compatibility between tribological surfaces and lubricant additives—*
12 *How friction and wear reduction can be controlled by surface/lube synergies*. Tribology
13 International, 2007. **40**(10–12), p. 1680-1695.
- 14 [6] Yue, W., et al., *Synergistic Effects between Plasma-Nitrided AISI 52100 Steel and Zinc*
15 *Dialkyldithiophosphate Additive under Boundary Lubrication*. Tribology Transactions, 2012.
16 **55**(3), p. 278-287.
- 17 [7] Ratoi, M., et al., *The Impact of Organic Friction Modifiers on Engine Oil Tribofilms*. RSC
18 Advances, 2014. **9**, p.4278-4285.
- 19 [8] Ma, Y., et al., *The synergistic effects of EP and AW additives with oxynitrided surface of*
20 *steel*. Tribology International, 1995. **28** (5), p.329-334.
- 21 [9] Khorramian, B.A., et al., *Review of anti-wear additives for crankcase oils*. Wear, 1993.
22 **169** (1), p.87-95.
- 23 [10] Tomaru, M., et al., *Effect of some chemical factors on film failure under EP conditions*.
24 Wear, 1977. **41**, p.117-140.
- 25 [11] Yamaguchi, A. “Tribology of Hydraulic Pumps,” in *Tribology of Hydraulic Pump*
26 *Testing*, Totten, G.E., Kling, G.H. and Smolenski, D.J., eds. American Society for Testing
27 and Materials, 1996. p. 49-61.
- 28 [12] Boßlet, J. *Tufftride/ QPQ Process*.
29 http://www.durferrit.de/media/pdf/Tenifer_QPQ_eng.pdf. [cited 2016 June]
- 30 [13] Xia, Y., et al., *Remarkable friction stabilization of AISI 52100 steel by plasma nitriding*
31 *under lubrication of alkyl naphthalene*. Wear, 2010. **268**(7–8): p. 917-923.
- 32 [14] Klueber Lubrication Munchen, *Bonded coatings for all metal surfaces*. p.1-16.
- 33 [15] Qiang, Y.H, et al, *Microstructure and tribological properties of complex nitrocarburized*
34 *steel*. Journal of Materials Processing Technology, 2000. **101**, p.180-185.
- 35 [16] Leite, M.V., *Wear mechanisms and microstructure of pulsed plasma nitrided AISI H13*
36 *tool steel*. Wear, 2010. **269**, p.466-472.

- 1 [17] Basso, R.L.O., *Effect of Carbon on the Compound Layer Properties of AISI H13 Tool*
2 *Steel in Pulsed Plasma Nitrocarburizing*. Plasma Processes and Polymers, 2007. **4**, p.728-
3 731.
- 4 [18] Kawamura, M., et al., *Organic sulphur and phosphorous compounds as extreme pressure*
5 *additives*. Wear, 1981. **72**, p.45-53.
- 6 [19] Wang, H., et al., *Micro and nano sulfide solid lubrication*. [Online]. Berlin: Springer,
7 2011. [Accessed 25 January 2016]. Available from:
8 <https://www.vlebooks.com/vleweb/Product/Index/678751?page=0>
- 9 [20] Guan, B., B.A. Pochopien, and D.S. Wright, *The chemistry, mechanism and function of*
10 *tricresyl phosphate (TCP) as an anti-wear lubricant additive*. Lubrication Science, 2016.
11 **28**(5): p. 257-265.