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The multiple roles of a chemical tribofilm in hydrogen uptake from lubricated rubbing contacts

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1. Abstract

A newly developed *in-situ* technique has been employed to investigate the effect of lubricant additives and water contamination in oil on hydrogen intrusion into the steel. Hydrogen in oil-lubricated contacts is generated as a result of tribochemical reactions. The hydrogen uptake measurement results indicated that tribofilm formation can impede hydrogen ingress, in the substrate, by impeding the formation of fresh metal surfaces. This reduces the generation of hydrogen atoms by preventing the decomposition of hydrocarbon molecules. A uniform tribofilm across the wear track also acts as a physical barrier for hydrogen permeating through the tribo-contact. The water contamination in the oil negatively influenced tribofilm properties and therefore led to higher permeation of hydrogen into the steel.

Keywords: Hydrogen permeation; *In-situ* measurement; Lubricant additives; Tribofilm; Water contamination

2. Introduction

Hydrogen embrittlement is a prevalent failure method, particularly in high-strength steels. Hydrogen atoms diffuse through the metal lattice and are trapped within irregularities such as grain boundaries, inclusions and dislocations. The accumulation of hydrogen beyond its solubility limit in these areas leads to the embrittlement of the steel. Hydrogen is also recognised as an influence on accelerating fatigue failure of tribological components by promoting White Etching Areas (WEAs), which are correlated to brittle flaking [1-3]. Studies on the detrimental effect of hydrogen showed an inverse relation between hydrogen content in steel and fatigue life of AISI 52100 bearing steel [4].

Previous investigations on hydrogen embrittlement in tribosystems revealed that hydrocarbon lubricants introduce a significant quantity of hydrogen into the contacting bodies [5]. The hydrogen atoms are liberated as by-product of the hydrocarbon molecules decomposition due to the high pressure, temperature and repeated shearing in the asperity contact [6]. The nascent surface generation in severe boundary/mixed friction contacts is responsible for accelerating hydrogen evolution [2, 5, 7]. The atomic hydrogen diffuses into the steel and subsequently induces cracks, leading to the premature failure of the component under the applied stress.

Hydrogen generation from lubricant decomposition highlights the importance of the lubricant additives which are used to improve physical and chemical properties of the base oil. Lu *et al.* [5] investigated a range of lubricant additives to reduce hydrogen evolution and found that phosphate-containing ionic liquid additives are the most effective in increasing the critical load for hydrogen liberation compared to the sulphur, nitrogen and phosphorous containing additives. The higher durability of the tribofilm formed in presence of this type of additive was the main reason of its improved performance. Research conducted by Niste et al. [8] recommended WS_2 nanoadditized lubricant as an effective solution to reduce hydrogen permeation into the steel. They attributed this behaviour to the presence of a complex WS_2 tribofilm and its potential to impede hydrogen permeation. Recent publications also reported that, in optimum conditions of temperature, pressure and sliding, the ZDDP-generated tribofilm can hinder hydrogen entry into the steel [9, 10]. The potential beneficial effects of DLC coating was also studied by Lu et al. [2] and it was found that the coating could prevent hydrogen permeation by reducing friction and wear led to the less chemical composition of the lubricant. Another study by Ooi et al. [11] suggested that black oxide coating acts as a barrier to hydrogen uptake from the lubricant.

Water contamination in the lubricant also represents an extra challenge for the tribosystems by generating hydrogen through the surface corrosion of metal [12]. Haque et al. [13] suggested that the formation of White Etching Cracks (WECs) is accelerated by adding water in the oil. They proposed that water in lubricant dissociates under friction and generates hydrogen causing WEC failure. The following reactions show the hydrogen evolution path through hydrolysis of corrosion products.

$$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^- \quad (1)$$

$$2H^+ + 2e^- \rightarrow 2H_{ads} \quad (2)$$

In the absence of oxygen, hydrogen can be generated according to reaction (3):

$$2H_2O + 2e^- \rightarrow 2OH^- + 2H^+ \quad (3)$$

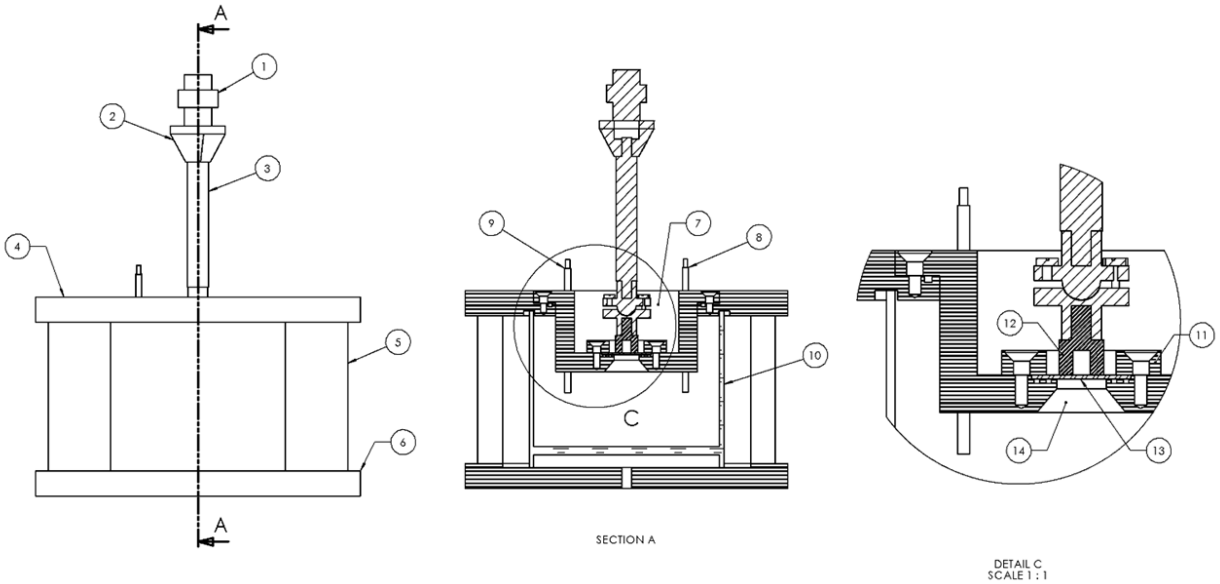
Although hydrogen embrittlement in mechanical components was the subject of interest in many research papers, there have not been many studies using *in-situ* techniques to monitor hydrogen uptake from a lubricated tribo-contact. In the limited studies that are available, the *in-situ* monitoring techniques were employed to measure hydrogen gas evolution from contact [5, 7]. Those techniques only measured the hydrogen molecules that desorbed from the surface as hydrogen gas without giving any information about hydrogen entry into the tribo-pair. A new real-time method was demonstrated by the authors in [14, 15] that can be employed to quantify hydrogen permeation into the steel from lubricated tribological contacts. This method is a combination of an electrochemical technique and a tribological contact and is based on a modified Devanathan-Stachurski (DS) setup.

The focus of this investigation is to understand the complex interplay between the lubricant composition and the tribofilm effect on hydrogen permeation rate. The newly developed technique, described in our previous paper [14], is used to determine whether lubricant formulation provides any improvement with regards to hydrogen uptake into the steel. The influences of two commonly used additives, zinc dialkyldithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC), as well as water contamination on hydrogen permeation rate were examined in this research.

3. Experimental procedure

3.1. Hydrogen uptake measurement

Figure 1 shows a schematic illustration of the developed apparatus that enables quantitative measurement of hydrogen permeation from a lubricated contact. This setup is made of a lubricated tribological part and an electrochemical hydrogen detection part. These two parts are separated by a thin steel membrane fastened and sealed at the bottom of the oil bath. Hydrogen is generated from the rubbing contact between the steel membrane and a metal counterpart. The larger amounts of hydrogen atoms on the surface of the steel leads to the diffusion of an unknown portion of the atomic hydrogen into the steel membrane. These hydrogen atoms are electrochemically oxidised and are detected once they emerge on the detection side of the steel [16]. The atomic hydrogen concentration on the detection side is kept negligible during the experiment by applying an anodic overpotential. More details of this technique have already been published in [14].



1. Load cell
2. Chuck
3. Shaft
4. Top plate
5. Pillars to bear the load
6. Base plate
7. Oil bath
8. Counter electrode
9. Reference electrode
10. Detection cell
11. Clamp to fix the membrane
12. Rubbing counterpart
13. Membrane – Working electrode
14. Exposure area

Figure 1: Schematic diagram of the hydrogen uptake apparatus.

A conventional three-electrode electrochemical system was utilized as the detection cell. The three electrode cell consisted of a platinum counter electrode in combination with Ag/AgCl reference electrode while the steel membrane is used as the working electrode. A compactstat Ivium potentiostat was employed to apply a constant overpotential of 115 mV *versus* the reference electrode in deaerated 0.1 Molar NaOH solution to oxidise the hydrogen atoms emerging on the output face. The sample was left until the background current density reached below 250 nA/cm^2 which is small enough to show any hydrogen diffusion during rubbing process. The oil of study (~125 ml) was added to the oil bath, on the hydrogen generation side. The oil was circulated with the flow rate of 25 ml/min through a heat exchanger continuously during the experiment. The lubricant was left until the temperature reaches 85±4°C and then the load was applied and the oscillation started. Table 1 summarizes the testing conditions. The oxidation current is continuously recorded every 10 seconds during rubbing. The captured data will be used to calculate the hydrogen permeation rate using Faraday's law. All measurements were performed at least two times to assure repeatability. The repeated results for the identical experiment conditions were within ±10% of the measured value in the steady state region of the curves. At the end of the test, the steel specimen was unmounted, ultrasonically rinsed with heptane and used for post-test analysis.

Table 1: Operating parameters.

Kinematics	Oscillatory motion
Load	70 N
Angular displacement amplitude	55 deg.
Temperature	85±4°C
Frequency	1 Hz
Test duration	5 hr

3.2. Sample preparation and materials

The material was an 800 µm thick membrane made of AISI 52100 bearing steel. The chemical composition of 52100 steel is presented in Table 2. Both sides of the specimen were polished with up to 1000 grit SiC polishing paper. A 40 nm thick layer of palladium were then deposited on one side of the membrane which will be exposed to the sodium hydroxide electrolyte. This film catalyses the hydrogen atom oxidation before they combine and form hydrogen molecules. This will improve the hydrogen detection efficiency of this method [17, 18].

Table 2: Chemical composition of AISI 52100 bearing steel (in wt%).

C	Mn	P	S	Si	Cr	Fe
0.95-1.10	0.25-0.45	0.025	0.025	0.15-0.35	1.35-1.65	Balance

The rubbing counterpart was a ring made of 303 stainless steel. Its chemical composition is presented in Table 3. The contact area of the running surface was 216 mm^2. The surface was roughened by machining to R_a=12 µm in order to promote boundary lubrication regime. The very large contact area and rough surface conditions were specifically employed to accelerate wear process and generate more hydrogen. Oscillatory motions occur between the membrane surface and the counterpart.

Table 3: Chemical composition of 303 stainless steel (in wt%).

C	Cr	Ni	P	S	Si	Mn	Fe
max 0.15	18	8	max 0.2	max 0.15	max 1	max 2	Balance

In order to contribute to the understanding of the role of the lubricant chemistry on hydrogen permeation rate, four different lubricant formulations (shown in Table 4) were tested in this study. Two well-known lubricant additives, ZDDP and MoDTC, were mixed with PAO base oil to investigate their basic mechanism of hydrogen uptake. The base oil has a kinematic viscosity of about 4.0 cSt at 100°C. The water-oil blend was prepared by injecting water into the oil and placing the container in an ultrasonic bath for 15 minutes to prepare the emulsified mixture.

Table 4: Lubricants tested and their formulation.

Lubricant	**Description**
PAO	Polyalphaolefin high purity, synthetic, non-polar base oil
PAO+ZDDP	P concentration: 0.08 %wt
PAO+ZDDP+MoDTC	P concentration: 0.08 wt%, 1 %wt MoDTC
PAO+ZDDP+Water	P concentration: 0.08 wt%, 5 %wt Water

3.3. Data analysis

The key features of a hydrogen permeation curve was already described in [14]. The hydrogen diffusivity and total amount of hydrogen permeated in the sample can be calculated from the permeation transient curves using mathematical analyses derived from Fick’s second law [16]. The following methods were utilised in this study to analyse the permeation transient curves. The background current is subtracted from the oxidation current value prior to using the equations 4 and 5.

- Time lag method

The time lag (t_{lag}) is calculated from the extrapolation of the hydrogen permeation transient plot. The t_{lag} (s) is the time required for the hydrogen permeation rate to attain 0.63 of the steady state value [19]. The effective hydrogen diffusion coefficient (D_{eff}) can be related to the t_{lag} by Equation (4):

$$D_{eff} = \frac{L^2}{6t_{lag}} \tag{4}$$

where D_{eff} represents a weighted average of the grain boundary diffusion coefficient and the lattice diffusion coefficient. *L* (m) is the thickness of the membrane.

- Total hydrogen permeation amount

The integration of the current density transients gives the total quantity of hydrogen permeated through the steel. Equation 5 defines the correlation between hydrogen permeation through the steel (mol/cm^{2}s) and the oxidation current density value [20]:

$$S = \frac{1}{Ft}\int_0^t idt \tag{5}$$

Where *i* is the current density (A/cm^2), *F* is Faraday's constant (96,485 C/mol) and *t* is the rubbing duration (s).

3.4. Surface characterisation

To investigate the hydrogen uptake mechanism of the tested lubricants, the wear tracks were physically and chemically characterised. Chemical characterization of the wear scar was carried out by Raman spectroscopy at the end of the tests. Raman analysis were carried out using a Renishaw InVia spectrometer (UK). The 488 nm wavelength laser operating at a maximum laser power of 10 mW at the source was utilised to obtain the spectra. The laser spot size is 800 nm in diameter. Different regions of the wear scar were analysed to ensure the uniformity of the surface layer. All Raman spectra reported here were obtained at room temperature within the range of 150-1670 cm^{-1}.

To achieve a better understanding of the performance of the lubricant additives, the wear volume of the steel membranes was measured using a white light interferometer (Bruker NPFLEX). The surface profile was measured at four different areas of the wear track to calculate the average wear width and depth of the specimen. This gives a good estimation of the average wear volume of each sample after 5 hours of rubbing.

4. Results

4.1. Hydrogen permeation test

The main objective of this work is to investigate the ability of tribofilm to reduce the permeation of hydrogen into steel by using an *in-situ* technique. The permeation curves for different lubricants as well as their corresponding total hydrogen permeation results are shown in Figure 2 and Figure 3, respectively. The hydrogen permeation results show that the tribo-contacts lubricated with any of the tested lubricants promote hydrogen uptake into the steel to some extent. It can be understood from the total hydrogen permeation results that the lubricant additives used in this study, ZDDP and MoDTC, reduce the hydrogen uptake into the steel when they were added to the PAO base oil. This contradicts our previous results reported in [14] where the experiments were conducted at room temperature. This observation highlights the effect of temperature on hydrogen permeation into the steel when the ZDDP additive was used. The higher hydrogen entry for ZDDP containing lubricant in comparison with that of PAO reported in [14] was correlated to the ZDDP decomposition by-products. It was explained that those products act as poisoning agents to inhibit hydrogen atom recombination. This subsequently led to a higher concentration of atomic hydrogen on the surface and thus hydrogen permeation becomes more likely before their desorption as hydrogen molecules [14, 15]. However, the smaller amount of permeated hydrogen for the ZDDP containing lubricant, in comparison with that of the pure base oil, at elevated temperature in this paper suggests that a different mechanism is involved in tribological hydrogen uptake.

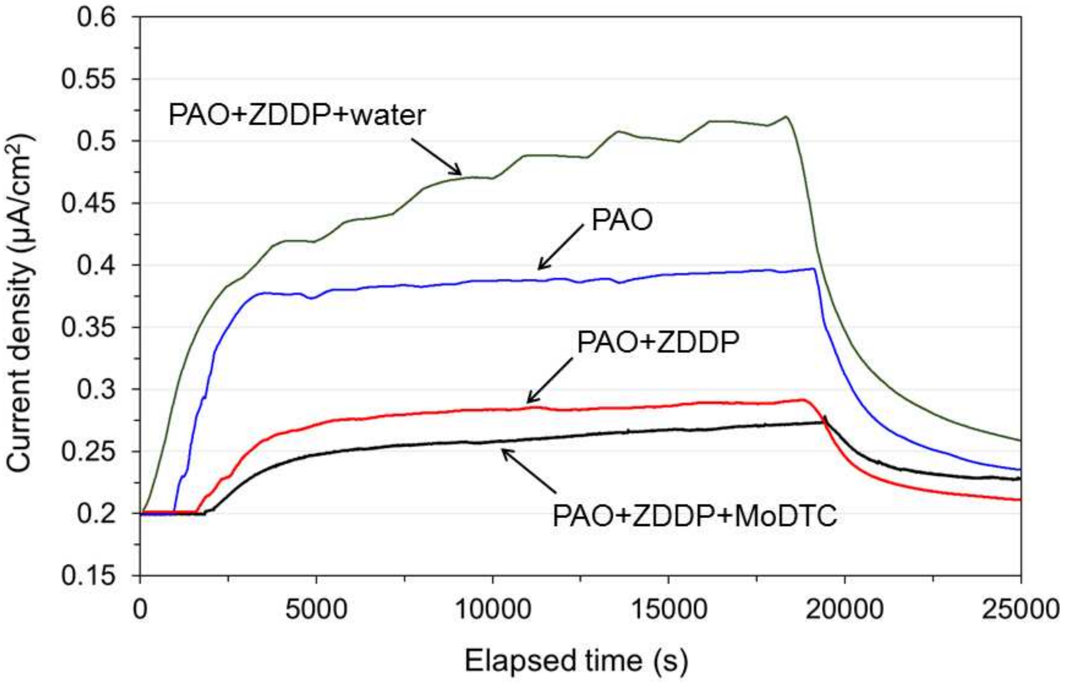


Figure 2: Effect of lubricant chemistry on hydrogen current transient during the test.

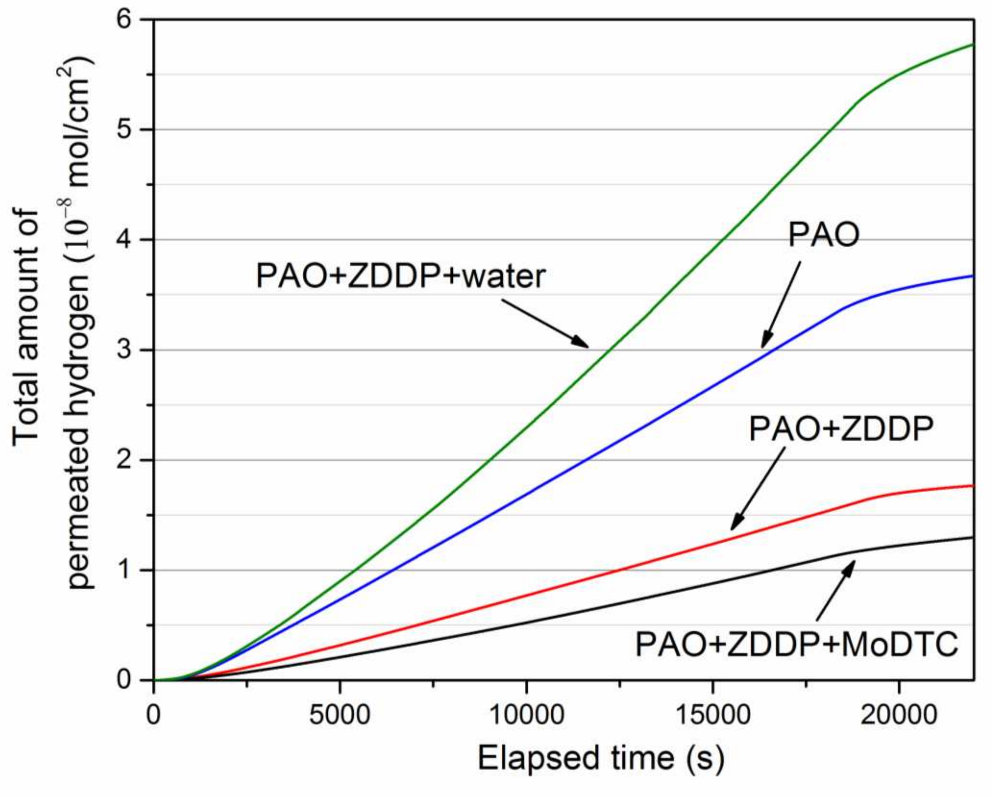


Figure 3: Effect of lubricant chemistry on total amount of permeated hydrogen through the membrane during surface-rubbing.

On the other hand, according to the results in Figure 2, the water contamination has a noteworthy influence on the hydrogen uptake. The increment of oxidation current density after oscillation has begun means that hydrogen evolved as soon as friction was commenced.

4.2. Surface analysis

The characterization of the surface layer is important in determining the effect of the tribofilm on hydrogen permeation into the steel. It is believed that the wear track is the main entry point for the hydrogen to permeate into the steel whilst negligible amount of hydrogen can enter the substrate from outside the wear track due to the passive oxide layer covering the surface [10]. Therefore, the surface analysis was conducted within the track. The Raman spectra acquired from the wear track of the samples tested by PAO, PAO+ZDDP, PAO+ZDDP+MoDTC and PAO+ZDDP+Water lubricants are shown in Figures 4 - 7, respectively.

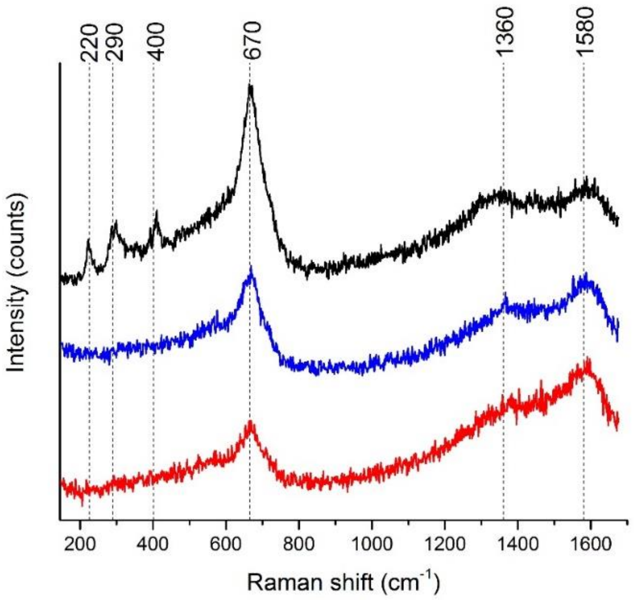


Figure 4: Raman spectra obtained from wear scars after testing with PAO lubricant.

The Raman spectra in Figure 4 reveals that the reaction film is composed of iron oxides, magnetite (Fe_3O_4) and hematite (Fe_2O_3), in some regions, within the wear track [21]. There are also additional broad peaks corresponding to amorphous carbon (D and G band signals at 1360 and 1580 cm^{-1}) [22]. The iron oxide layer is readily removed during mechanical wear and fresh metal sites are formed. Therefore, no protection should be expected from this layer in comparison with that provided by a tribofilm.

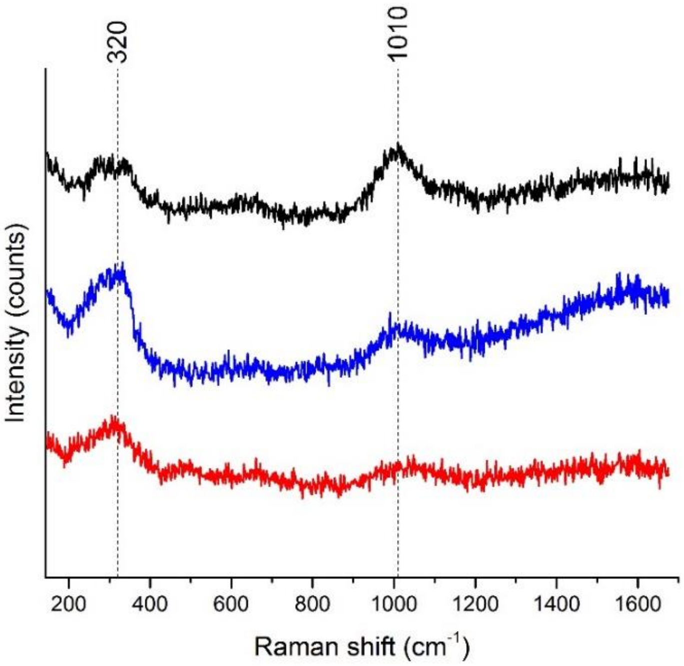


Figure 5: Raman spectra obtained from wear track after testing with PAO+ZDDP lubricant.

The ZDDP tribofilm is identified within the wear track of the sample tested with PAO+ZDDP. The broad peak observed in the region of 900-1100 cm^{-1} in Figure 5 confirms the phosphate compounds within the tribofilm [23]. The broad peak at 200-400 cm^{-1} also belongs to iron sulphide [24]. Glaeser et al. [25] have already reported the formation of iron sulphide within the boundary film in the contact region due to the high contact pressure. They highlighted the importance of the sulphide film (6-10 nm thick) in preventing asperity-asperity contact and inhibiting adhesive wear. According to Bell et al. [26], iron sulphide formation is promoted through the reaction of sulphide products from decomposition of ZDDP with the metal surface. It is also suggested that the adhesion between the phosphate layer (on top) and the metal surface (on bottom) is improved in the presence of the metal sulphide [26].

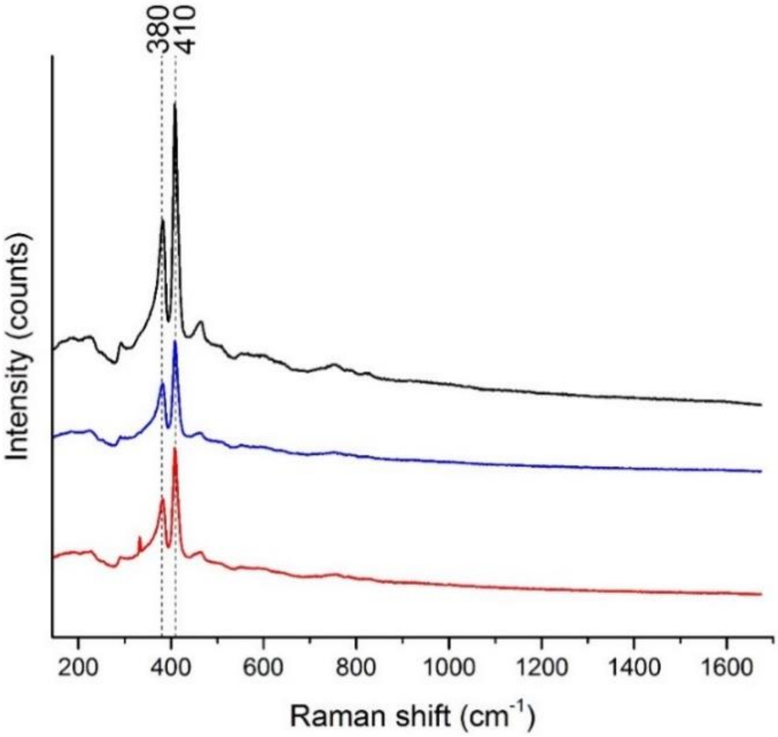


Figure 6: Raman spectra obtained from wear scar after testing with PAO+ZDDP+MoDTC lubricant.

Raman spectra from the generated wear on the sample tested with PAO+ZDDP+MoDTC lubricant (Figure 6) exhibited the main signals for MoS_2. The peaks at 380 and 410 cm^{-1} correspond to MoS_2 and the broad peak around 200 cm^{-1} is correlated to the stress-induced crystalline disorder of MoS_2 structure within the tribofilm [27]. The MoS_2 hexagonal crystal structure is known as the shear-induced MoDTC decomposition product [28]. The weak coulombic force between the molybdenum atomic layer and the sulphur atomic layer in the MoS_2 structure is desirable to reduce friction [29].

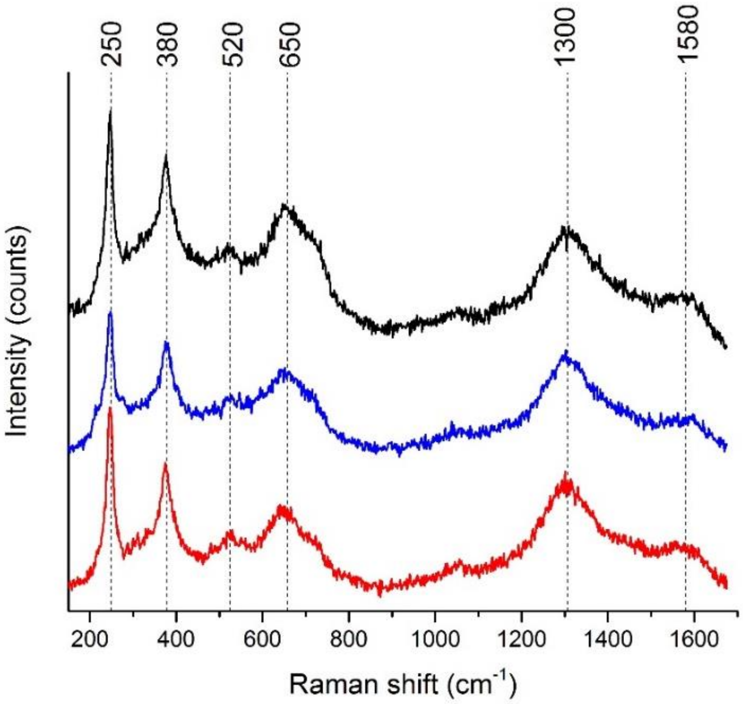


Figure 7: Raman spectra obtained from wear scar after testing with PAO+ZDDP+water lubricant.

On the other hand, the Raman spectra obtained from the sample tested with PAO+ZDDP+water show no indication of the formation of phosphate tribofilm. This is in line with what we already know from the literature, that interaction between water and ZDDP additive affects the tribochemical reactions in a lubricated tribo-contact [30]. The Raman spectra in Figure 7 also identify the amorphous carbon on the surface of the sample tested with water contaminated lubricant.

4.3. Wear results

As reported in numerous publications, nascent surface generation is one of the most influential factors on hydrogen evolution from a tribo-contact. It is believed that hydrocarbon lubricants are decomposed through a series of steps initiated by sliding contact [31]. This is followed by the adsorption of the hydrocarbon molecules to the fresh metal surface generated by mechanical stimulation. The material defects generated through wear processes on the surface are believed to exacerbate decomposition of the lubricant [31, 32]. Hence, the wear rate can control the hydrogen evolution from the surface through the lubricant decomposition rate. Not unexpectedly, total wear volume results in Figure 8 show the positive effect of lubricant additives on reducing wear. The lowest wear volume value was observed for the

PAO+ZDDP+MoDTC lubricant. The formation of the chemical tribofilm accounts for the reduced wear seen in presence of the lubricant additives. The lower hydrogen permeation measured for the additive-containing lubricants is also partially related to the lower wear volume of those tests. The wear volume slightly increased for water contaminated lubricant in comparison with that of the PAO+ZDDP. Despite the relatively low wear observed with PAO+ZDDP+water tested sample, the highest permeation rate of hydrogen was measured for this lubricant (Figure 8). This suggests that a different mechanism is involved in hydrogen permeation into the substrate in presence of water. This will be discussed further in the Discussion section.

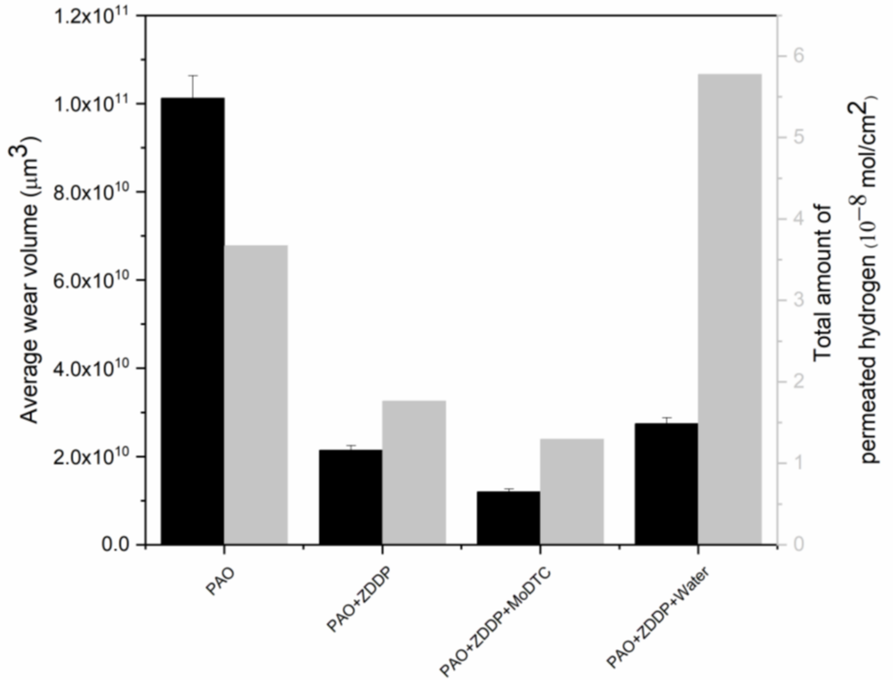


Figure 8: Total amount of permeated hydrogen and the wear volume of the samples tested by different lubricants at 85°C.

5. Discussion

The effective hydrogen diffusivity values were determined using the time-lag method and they were $(1 \pm 0.5) \times 10^{-10}$, $(7 \pm 0.7) \times 10^{-11}$ and $(6 \pm 0.5) \times 10^{-11}$ (m^2/s) for PAO, PAO+ZDDP and PAO+ZDDP+MoDTC, respectively. These values have been verified against literature data [33, 34]. Diffusion coefficient is constant for a material at a given temperature. However, a degree of uncertainty is expected in this technique due to the changes in the membrane thickness during sample polishing. The smaller coefficient of hydrogen diffusion within the tribofilm compared to its value through steel, is another possible reason for the smaller effective hydrogen diffusivity values in additives containing lubricants. Preventing hydrogen diffusion into the steel using surface layers containing nickel and tungsten were also reported in previous research [35, 36].

The permeation current density did not reach steady state for the water contaminated lubricant and therefore the hydrogen diffusion coefficient could not be calculated. The high formation rate of corrosion products in presence of water and their continuous removal due to the rubbing cycles will result in non-uniform permeation of hydrogen and a, consequently, non-steady permeation current.

There are three consecutive steps in the hydrogen permeation experiments. First, the hydrogen is generated at the tribological side of the membrane and enters the steel. Second, the atomic hydrogen transports through the metal membrane. The passage of the hydrogen atoms is hindered by the lattice defects that tend to attract and confine some of the hydrogen atoms in the steel until a saturation point is reached and the rest of the hydrogen atoms exit at the detection side. Finally, the emerged atoms are oxidised by the applied anodic potential. The schematic illustration of this mechanism is presented in Figure 9.

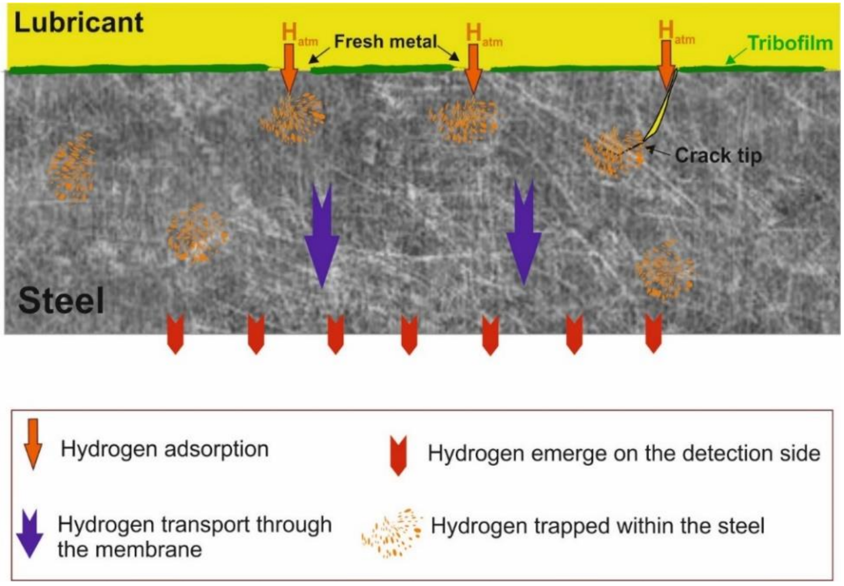


Figure 9: Schematic illustration of the hydrogen entry into the steel, its diffusion and emerging on the detection side during surface rubbing.

The permeation samples used for our experiments were all prepared through the same procedure and the hydrogen transportation inside the metal remained undisturbed. Furthermore, the hydrogen atoms are oxidised instantaneously at the detection side of the sample. Therefore, it can be assumed that the total hydrogen permeation and hydrogen flux values measured in this technique are entirely ascribed to the intensity of hydrogen generation/entry rate.

The hydrogen entry into the steel is controlled by the adsorbed hydrogen atoms coverage (θ_H) of the surface. It also correlates to the transfer rate of hydrogen from the adsorbed state to the absorbed state in the subsurface layer. The bonds formed between the fresh metal surface and hydrogen are very strong. Thus, the high θ_H only takes place when a significant removal of the oxide layer leads to the fresh metal exposure to the lubricant. Accordingly, the higher hydrogen flux is expected when the wear rate is high, not only because of the strong bonds between hydrogen atoms and the nascent surface, but also due to the catalytic action of fresh metal surface on lubricant decomposition [2, 5, 7, 8, 31]. The latter was reported as a crucial parameter for organic materials decomposition and generating hydrogen by several researchers [5, 31]. Thus, the lubricant additives play an important role in hydrogen uptake into the steel by controlling the wear rate.

Raman spectroscopy results confirmed the formation of a uniform phosphate tribofilm and metal sulphides on the surface of the sample tested by PAO+ZDDP. The lower wear for the ZDDP-containing lubricant is explained by the wear protection characteristics of this thermo-shear induced phosphate film formed by the decomposition of ZDDP additive [37]. The lower wear volume of this lubricant led to the lower hydrogen uptake. This inhibition mechanism is provided by deactivating the catalytic effect of fresh metal and thus reducing the degradation rate of hydrocarbon molecules. The strong interaction between the rapidly forming tribofilm and the metal substrate will cause less metal-metal contact at asperities and fewer active sites to be exposed during rubbing process. The correlation between the tribofilm formation and decomposition rate of the lubricant was already suggested by other researchers [5, 8, 9]. Both Niste et al. [8] and Tanaka et al. [9] pointed out that ZDDP tribofilm can prevent hydrogen embrittlement by interfering with the production of atomic hydrogen on the nascent surface. The differences between the Thermal Desorption Spectrometry (TDS) *ex-situ* technique used in those studies and the *in-situ* measurement employed in the current research make comparative studies difficult. However, Tanaka et al. [9] showed that the ZDDP containing lubricant can reduce the hydrogen permeation amount by 50% in a 10-hour experiment which is compatible with the total hydrogen uptake value obtained from this present study (Figure 3).

The comparison of the results in this paper and our previous experiments conducted at room temperature [14] show that the tribofilm effectiveness in preventing hydrogen permeation into the steel is strongly dependent on the temperature. This finding was also reported by Niste et al. [10] and it was explained that the coverage of the surface by the tribofilm at low temperatures is inadequate to inhibit hydrogen permeation. They showed that ZDDP tribofilm can either facilitate or mitigate hydrogen permeation into the steel depending on its homogeneity. A uniform tribofilm such as the one formed for ZDDP containing additive in this research could restrain hydrogen entry by blocking the surface and reduce the hydrogen permeation rate. In contrast, the combined action of larger wear and poor coverage of the surface promote hydrogen permeation into the steel at room temperature in presence of ZDDP additive. Furthermore, a series of papers have shown that the ZDDP decomposition by-products such as sulphur and phosphorus act as poisoning species for recombination of hydrogen atoms on the metal surface [14, 15, 38, 39]. This leads to the higher permeation of hydrogen where there is no uniform tribofilm formed on the surface. This highlights the importance of the heat induced-tribochemical reactions at elevated temperature that promote the homogeneity and increase the thickness of the tribofilm. According to previous findings, elevated temperature accelerates ZDDP decomposition [40-42] and this appears to be a reason for the formation of a more uniform tribofilm in this study compared to the experiment results conducted at room temperature [14]. Niste et al. [10] investigated the importance of temperature in generating ZDDP tribofilms and found that higher temperatures promoted uniform films that can exert a beneficial effect in reducing hydrogen permeation in rubbing contacts. This is in line with another study that found ZDDP chemisorption starts only above 50°C [43]. Barcroft et al. [44] also suggested that high temperature is essential for tribofilm formation. Their results confirmed tribofilm deposits at asperities where the temperature is high whereas in the regions between the asperities a heterogeneous amorphous thiophosphate formed.

Another explanation is related to the multilayer tribofilm with a glassy phosphate layer on the top acting as a physical barrier for hydrogen permeating through the wear track. The similar performance was already reported for WS_2 additive which blocks hydrogen permeation through the wear track by generating a durable tribofilm [8]. The multilayer structure of ZDDP tribofilm consists of a solid layer strongly adhered to the metal substrate and a semi-solid layer weakly adhere to the solid layer [45]. It is assumed that the top layer limits the hydrogen access to the bottom sulphide layer and controls hydrogen permeation.

The results in Figure 3 also show the affirmative effect of MoDTC additive on hydrogen permeation into the contacting surfaces. Further reduction of hydrogen uptake was observed in presence of MoDTC. The positive effect of MoDTC resides in the formation of MoS_2 crystal identified by Raman spectroscopy [28]. The synergistic effect between ZDDP and MoDTC could promote the tribofilm growth within the wear scar. The improved performance of the combination of ZDDP and friction modifier additives were thoroughly investigated elsewhere [37, 46]. These favourable properties make MoDTC a promising candidate additive to combine with ZDDP to impede permeation of hydrogen into steel.

Hydrogen permeation results in Figure 3 showed the concomitant effects of water and ZDDP in the lubricant on increasing the total amount of hydrogen permeated into the specimen by more than 300% as compared to the PAO+ZDDP oil. Water content measurement in the oil by a titration-based technique, the Karl Fischer method, showed that most of the water was removed from the lubricant by evaporation. This implies that water affects hydrogen permeation rate even if exists in small amounts in the PAO+ZDDP lubricant for a brief period of time. As observed from the Raman spectra in Figure 7, no tribofilm is identified on the surface of the sample tested by PAO+ZDDP+water. This indicates that water contamination disturbs the mechanism by which ZDDP additive blocks hydrogen entry. However, the relatively low wear observed for the water contaminated lubricant suggests that the tribofilm is present. Therefore, the film is either partly formed or partly worn off leading to a very patchy tribofilm that only covers certain areas. As a result, this film is able to reduce wear but it is not uniform enough to mitigate hydrogen permeation leading to the largest amount of hydrogen permeation into the steel. Furthermore, water contamination in combination with sulphur species promotes hydrogen permeation into the steel by generating H_2S according to the reaction (6) proposed by Spedding et al. [47].

$$-P = S + H_2O \rightarrow -P = O + H_2S \qquad (6)$$

It is very well known that hydrogen sulphide accelerates premature failures by promoting hydrogen embrittlement [38, 48-50]. The higher hydrogen atoms surface coverage is plausible in presence of H_2S due to the higher corrosion rate and its detrimental role in extending the time for hydrogen atoms recombination on the surface.

Based on the aforementioned argument, a ZDDP tribofilm with a layered structure formed across the wear track offers beneficial effects through a number of mechanisms. The formation of a uniform tribofilm at high temperature reduces hydrogen production by deactivating the catalytic action of nascent surface and diminishing the active sites on the surface. The tribofilm also acts as a physical barrier blocking hydrogen diffusion into the steel. Conversely, the hydrogen permeation results presented in our previous paper [14] showed that the tribofilm formed at room temperature is not uniform enough to inhibit hydrogen permeation into the steel. Further reduction of hydrogen permeation was observed when MoDTC were added to the lubricant. This was attributed to the active role that MoDTC plays in combination with ZDDP to enhance the tribofilm growth within the wear scar which is an effective obstacle to the entry of hydrogen. On the other hand, an inadequate coverage of the surface by tribofilm in presence of the water contamination allows significant permeation of hydrogen into the steel.

6. Conclusion

A new *in-situ* monitoring technique was utilised to explore the influence of lubricant composition on hydrogen uptake from a tribological rubbing-contact. This method provided a reliable means for determining lubricant additives that have the potential to mitigate the hydrogen permeation into the steel. This paper highlighted the role of ZDDP and MoDTC additives as well as water contamination on hydrogen permeation into the steel. The results indicate that the lubricant formulation has a potent effect on hydrogen permeation rate into the steel. A significant reduction of hydrogen entry was observed for both ZDDP and MoDTC-containing lubricants compared to that of the PAO base oil. The physical barrier effect of a uniform tribofilm and the reduction of the nascent surface are the most important causes for the lower hydrogen permeation in presence of the ZDDP anti-wear additive. The further reduction of hydrogen permeation was observed in experiments with the MoDTC-containing lubricant. This beneficial role is ascribed to the synergistic effect of MoDTC with ZDDP during the growth of the tribofilm. It was also suggested that water contamination facilitates the entry of hydrogen into the metal by damaging the tribofilm. The insights from this research are in line with the current state-of-art findings that provide a new strategy for combating hydrogen embrittlement in tribological applications by introducing the right additive chemistry to control the hydrogen uptake.

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