Effect of Zinc Dialkyl Dithiophosphate Replenishment on Tribological Performance of Heavy-Duty Diesel Engine Oil

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Abstract

Soot is the main contamination that affects oil performance and increases oil drain intervals in heavy-duty engine oil. It is also believed that additive concentration in engine oil can be influenced due to additive depletion over time and additive adsorption on soot particles. To extend oil drain intervals and improve oil performance, filter manufactures explore removing the soot to a certain level and replenishing the consumed additives. Zinc Dialkyl Dithiophosphate (ZDDP) is one of the most favoured anti-wear additives that reacts very rapidly with rubbing surfaces to form tribofilm that reduce wear. In this study, the experimental work aims to investigate the effect of ZDDP replenishment on tribological performance in the existence of soot and after removing soot from heavy-duty used oil. The study reveals that reclaiming the used oil can be achieved by removing the soot to a certain level. The results demonstrate that the reclaimed oil after removing soot is still not as good as the fresh oil. This study proves that additive depletion, additive adsorption on soot and the decomposition of antiwear additive adversely influence the reclaimed oil performance. However, replenishing the consumed additive by adding a small amount of ZDDP helps to improve the reclaimed oil performance compared to a large amount of ZDDP which is required to re-gain the oil performance in the existence of soot.

Keywords/Phrases
Soot, Wear, Additive depletion, Additive replenishment

1. Introduction

Engine manufacturers are growing demands to increase the oil drain interval. The U.S. reported\textsuperscript{1} that over 1 billion gallons of lubricants annually are replaced in light vehicles and more than 250 million gallons in trucks. Engine manufactures are under considerable pressure to reduce the effects of disposal oil on the environment and improve profitability by extending the service life of engine oils\textsuperscript{1}. Soot is the main contamination that influences significantly oil drain interval in diesel engines\textsuperscript{2,3}. The effects of soot on the oil performance have been addressed by several studies; some researches focused on the effect of soot on wear\textsuperscript{4-5}, other studies concentrated on soot effect on tribofilm and rubbing surfaces\textsuperscript{9,10} and finally, additive adsorption on soot particles has been the topic of interest\textsuperscript{3,11-14}. Presence of soot in diesel engine oil is one of the most common reasons to change engine oil
While removing soot by filters can improve the oil functionality, however, there is still depleted additives that needs to be replenished to enhance the oil performance.

Additives in engine oils could be consumed, decomposed or depleted after being used in the engine causing a decrease in the oil performance. Engines manufacturers recommend that engine oil should be changed at regular intervals depending on the operating conditions to keep the additive level up. Replenishing these additives can forestall oil degradation and maintain oil properties and its effectiveness for a longer time. In order to prolong the oil change intervals, It has been proposed to add an excess amount of additive to ensure a sufficient quantity of additive exists at all time. The additives are suggested to be added periodically regardless of oil contaminants or the oil usage history. Replenishing the additives can protect the contacts surfaces from abrasive wear caused by soot and prevent oil oxidation and corrosion.

Zinc dialkyldithiophosphates (ZDDPs) is the most common additive which can control wear and act as oxidation and corrosion inhibitor. ZDDP reacts on rubbing surfaces to form a quite thick tribofilm (up to 200nm). The effect of ZDDP concentration on tribofilm formation was investigated by Yin et al. The results revealed that a low concentration of ZDDP (0.25wt% and 0.5wt%) forms short phosphate chains, whereas a high percentage of ZDDP (1% and 2%) leads to the formation of long phosphate chains. Furthermore, Tomala et al. found that the larger percentage of ZDDP causes thicker and larger roughness of tribofilm. Ghanbarzadeh et al. indicated that increasing ZDDP concentration increased the formation and thickness of tribofilm and reduced the wear. The formation of tribofilm derived from added ZDDP has a negative effect on friction causing an increase in friction coefficient. The reason behind this is the higher shear strength of tribofilm due to an effective roughening of rubbing surfaces by the formation of uneven distribution of asperity peaks.

Additive replenishment is an interesting topic to the manufacturing sector since it can potentially extend the lubricant’s life. There are many studies regarding the effect of adding additives on fresh oils to enhance the oil functionality, while the effect of additives replenishment on used oil or reclaimed oil has not been investigated. However, several patents have discussed different additive system suppliers to replenish the consumed additives through controlled injectors or filters. Some patents designed oil filters to release additives using such as colloidal suspensions of PTFE particles with a size less than two microns in filter. Polyolefin container or capsules containing additive is studied to release the additive in flowing oil. Soluble composite in filter material such as polymer matrix is used to release the additive. Other patents suggested mechanical mechanisms that can inject the additive into oil circulation systems. All of these techniques have not taken into account that adding too much additive has a negative effect on tailpipe emissions and the vehicle fuel...
economy. Accordingly, it is important to have a controlled additive technique to keep the additive concentration within the desirable limits.\cite{35}

In the current study, the ZDDP replenishment process in heavy-duty used oil containing soot and after removing the soot is explored. ZDDP is added to used oil to overcome the negative effects caused by soot particles and the additive depletion in the engine. This study determines the amount of the depleted additive and the level of ZDDP needed to extend the service life of heavy-duty used oil in the existence of soot or after reclaiming the used oil by removing soot.

2. Experimental methodology

2.1 Materials and method

Fully formulated oil (BDS4) of heavy-duty vehicles with viscosity grade 15W40 was used in this study. The physical and chemical properties of fresh oil are displayed in Table 1. The engine oil after being used in the heavy-duty diesel engine of a truck was drained for further investigations. The drained oil was provided by Parker. The mileage details of drained engine oil are shown in Table 2. Chemical investigation to study the oil degradation was conducted using Fourier-Transform Infrared Spectroscopy (FTIR). FTIR results demonstrate the change in the oil after being used as shown in Figure 1. Figure 1 reveals two interesting areas in the used oil spectrum compared to the fresh oil. The 978 cm\(^{-1}\) point is correlated to the P-O-C bond which refers to the antiwear additive and the 2000 cm\(^{-1}\) point relates to soot level in used oil.\cite{36} Figure 2a shows no peak in used oil at 978 cm\(^{-1}\) point that could be due to depletion or decomposition of antiwear additive. Decomposition of antiwear additives at engine conditions was found in previous studies.\cite{18,52} Figure 2b confirms the existence of soot particles in the used oil as there is a shift in the FTIR spectra at 2000 cm\(^{-1}\).

Table 1: Physical and chemical properties of fresh oil.

| Details                        | Parameters       |
|-------------------------------|------------------|
| Density at 15°C                | 0.874 g/ml       |
| Kinematic viscosity at 40 °C   | 113 mm\(^2\)/s   |
| Kinematic viscosity at 100 °C  | 15 mm\(^2\)/s    |
| Flash point                    | 215 °C           |
| Total base number              | 10 mgKoH/g       |
| Zn concentration               | 1306 ppm         |
| P concentration                | 1158 ppm         |
| S concentration                | 6366 ppm         |
| Ca concentration (ppm)         | 1332 ppm         |
Inductively Coupled Plasma (ICP) has been used to further investigate the change in additive concentration in the used oil. ICP analysis was conducted at Oil Check Laboratory Services Ltd, UK.

Table 2: Used oil details.

| Truck   | Fill (21.6.19) | Drain (29.11.19) |
|---------|----------------|------------------|
| Mileage | 524604 km     | 563842 km       |

Figure 1: FTIR chemical analysis of used oil compared to fresh oil.
2.2 Soot removal by centrifugation

A centrifuge was used to remove soot particles from the used oil. The centrifuge was conducted at 40°C with a speed of 12000 rpm for 2hrs. This centrifugation process was repeated six times to ensure that most of the soot has been removed. FTIR was used to measure the soot level in the used oil according to ASTM D7844 standard. Figure 4 shows the calibration curve to estimate soot percentage in used oil plotted between different levels of carbon black (CB) and the shift at the 2000 cm⁻¹ point. A full explanation of the calibration curve method to determine soot percentage was described by Bordg H et al. The calibration curve was applied in this study to measure the soot level in drained oil after every centrifuge run. Figure 3 shows a decrease in soot percentage in used oil after every run as the FTIR spectra shift up. Drained oil contained 0.62 wt% of soot after being used in the truck. Soot level decreased gradually after every centrifuge run and the soot level after 6-times centrifugation became 0.05wt% as shown in Figure 4.

Figure 3: Centrifugal process was repeated 6-times at the same conditions and soot level was measured after every run, the shift at 2000 cm⁻¹ point was used to estimate the soot percentage in used oil.
2.3 ZDDP replenishment process

ZDDP antiwear additive at different levels was used in this study to replenish the consumed additive at both conditions before and after the removal of soot. For all oil samples, a magnetic stirrer was used to mix the ZDDP homogeneously into the oil at 60°C for 30mins. The experimental matrix of tribological tests is shown in Table 3.

Table 3: The details of tribological tests program after the replenishment process.

| Tested oils         | ZDDP replenishment (wt%) |
|---------------------|--------------------------|
|                     | 0  | 0.75 | 1.5 | 3   | 5   |
| Used oil            | ●  | ●    | ●   | ●   | ●   |
| Reclaimed oil       | ●  | ●    | ●   | ●   | ●   |
2.4 Tribological test

TE77 tribometer has been used to simulate reciprocating sliding contacts in the engine according to ASTM G 181 \[^{39}\]. Table 4 shows the test conditions used in the experiments to investigate the tribological performance of tested oils in boundary lubrication regime (Lambda of FFO $\lambda=0.27<1$) \[^{40}\]. The specification of the pin and plate is described in Table 4. The pin is normally loaded against the stationary plate. The oil temperature is kept at 100°C to replicate the real working condition in the engine.

Table 4: TE77 set up parameters and materials properties of specimens.

| Material Properties     | Pin          | Plate         | TE77 Parameters              | Value |
|-------------------------|--------------|---------------|------------------------------|-------|
| Material                | Steel EN31   | Steel EN31    | Temperature °C              | 100   |
| Dimensions (mm)         | 10 radius    | 7x7x3         | Contact pressure (GPa)      | 1.26  |
| Hardness (HRC)          | 58-62        | 58-62         | Load (N)                     | 22.1  |
| Roughness (nm)          | 30-50        | 400-600       | Frequency (Hz)               | 25    |
| Elastic modulus (GPa)   | 190-210      | 190-210       | Test duration (min)          | 120   |
| Poisson’s ratio         | 0.28         | 0.28          |                              |       |

An optical white light interferometer (NPFLEX) was used to measure wear on pins after the tribological test. The size of the scar on pin was determined by Vision64 software after analysing the scanned images. Wear volume loss (spherical cap volume) on pin is calculated using the equations (1) and (2) as follows:

\[
V_{\text{pin volume loss}} = \frac{\pi h^2 (3R - h)}{3} \quad (1)
\]

\[
h = R - \left( (R^2 - r^2) \right)^{0.5} \quad (2)
\]

Where,

$R$: sphere radius (µm), $h$: Spherical cap height (µm), $r$: wear scar radius (µm).

Scanning Electron Microscopy (SEM) technique was used to analyse the surface of wear scar by providing detailed high-resolution images. Energy Dispersive X-ray (EDX) analyser was applied in this study to identify the chemical compositional of tribofilm.

3. Results and discussion

3.1 Soot removal effect on used oil performance

Soot in real engine oil has been investigated in several previous studies \[^{4-8}\] to determine its effects on wear. The results showed an increase in wear as the soot level increased in the oil. Conversely, removing soot from used oil decreases its effect on wear. In this study, the centrifuge process was repeated 6-times at the same conditions and soot level after each run was measured by FTIR. Figure 5 shows a decrease in soot level by repeating the centrifuge process. As the soot level in used oil decreased, wear also decreased as expected to reach stable wear values after 4-centrifuge runs which no further decrease in wear. It is worth noting that wear after removing soot is still higher than the
wear of fresh oil sample. This can be due to the additive adsorption on soot and/or antiwear decomposition as FTIR results showed in Figure 2a. As there was no change in wear values after 4-centrifuge runs, thus the used oil after 4-centrifuge runs is used for further additive replenishment tests. Soot level in used oil was 0.62wt% after draining the oil from the truck and reduced to 0.26wt% after 4-centrifuge runs. The results are in line with study 41 confirmed the low level of soot (0.2wt%) in engine oil does not have a significant effect on wear and agreed with other studies 48–50 found that removing the soot from used oil reduced its effects on wear.

![Figure 5: The effect of repeating the centrifuge process on both soot level and wear.](image)

### 3.2 Additive depletion in used oil

ICP chemical analysis was conducted for used engine oil (0.62wt% soot) and reclaimed oil after removing soot. Figure 6 indicates the change in the concentration of oil additive after being used in the engine as expected. The results show a decrease in the additive concentration of Zn, P, S and Mg except Ca concentration. Zn, P and S elements come from the antiwear additive, such as Zinc dialkyldithiophosphate, and it is expected to be consumed to protect the tribological surfaces. P and S elements could also come from dispersant/detergent compounds such as sulfonates and phosphonates 42. The function of detergent is used to clean and neutralize oil impurities 42. Ca and Mg elements originate from the detergent compounds. Figure 6 shows an increase in Ca level after being used in the truck. This could come from impurities, rainwater, fuel or road dust. There is a significant drop in Mg concentration that may be used to overcome impurities and other contaminants that caused an increase in the Ca level.
Additives adsorption on soot particles has been studied before $^{3,11-13}$. Thus, there is a possibility of removing the additives that are adsorbed on the soot particles during the centrifugation process $^{43}$. Additive adsorption on soot was observed in this study after removing soot as shown in Figure 6. In general, there was a decrease in the concentration of all elements that originated from both antiwear and dispersant/detergent. The results agree with several studies $^{3,11-13}$ that investigated additives adsorption on soot. However, the effect of additive depletion and additive adsorption on oil performance has not been investigated in previous studies $^{3,11-13}$.

![Figure 6: ICP chemical analysis of fresh oil, used oil and reclaimed oil (after removing soot).](image)

3.3 ZDDP replenishment of used oil

3.3.1 Chemical analysis of oils

Used engine oil was drained after approximately 40,000 km of driving as shown in Table 2. ICP analysis of used oil showed a decrease in most additive elements concentration due to additives depletion as shown in Figure 6. ZDDP was used in this study to replenish the consumed additive in the used oil and improve its tribological performance. As known ZDDP contains three main elements Zn, S and P, adding ZDDP to used oil will increase the concentration of these elements. ICP analysis after adding different levels of ZDDP was conducted as shown in Figure 7. The results show an increase in the concentration Zn, S and P with no change in Ca and Mg. As the level of ZDDP increases in the used oil,
the higher performance of used oil is expected to improve. ZDDP promotes the formation of antiwear tribofilm to protect the rubbing surfaces from oil contamination.

![Figure 7: The concentration of additive elements in used oil after adding different levels of ZDDP.](image)

### 3.3.2 Tribological performance

Tribological tests of used oil before and after adding different levels of ZDDP have been conducted as shown in Figure 8. In this study, there is the synergy of two main mechanisms that influence wear and affects the oil functionality after being used in the truck. Firstly, additive depletion or decomposition of antiwear additive that consumed or decomposed in used oil over time causes an increase in wear as illustrated in Figure 1. Secondly, the existence of 0.62wt% soot influences tribological performance and causes hard abrasive wear on the rubbing surfaces. After replenishing depleted additives in the used oil, the results demonstrate a consistent decrease in wear with the increase in the level of ZDDP in used oil. Figure 8 reveals that wear of used oil after adding 3 wt% ZDDP performs almost similar to the fresh oil. In this study, it can be concluded that replenishing used oil by adding 3wt% ZDDP or more was sufficient to renew the oil functionality even in the existence of 0.62wt% soot.

On the other hand, the soot effect on friction is negotiable depending on the soot level in the oil. The higher level of soot can cause oil starvation and an increase in friction coefficient. While it has
been observed a decrease in friction coefficient with low soot level as soot particles act as friction modifier \(^{44}\). In this study, the friction coefficient of used oil contains 0.62 wt% soot decreases before adding ZDDP as shown in Figure 8. Soot acts as a friction modifier causing a decrease in friction coefficient. The results in line with studies \(^{44,45}\) demonstrated the effect of soot on friction in the existence of soot at low-level. As ZDDP is added in the oil, a higher friction coefficient resulted \(^{25,26}\). The higher friction coefficient after adding ZDDP can be explained due to the formation of tribofilm derived from ZDDP. The reason behind this is the higher shear strength of tribofilm \(^{25}\) due to an effective roughening of rubbing surfaces by the formation of uneven distribution of asperity peaks \(^{26}\). The friction coefficient starts levelling when 1.5wt% ZDDP or more exists in the used oil as shown in Figure 8. It appears that tribofilm roughness had a limiting effect on friction with a ZDDP level of ≥1.5wt.

![Figure 8: Wear and friction of used oil after adding different levels of ZDDP.](image)

### 3.3.3 Surface analysis

Previous studies \(^{9,10}\) revealed that soot in engine oil causes abrasive wear on rubbing surfaces. Figure 9 shows SEM images of wear scar on pins of used oil and after adding ZDDP at different levels. It is expected to see abrasive wear on the surface of used oil in the existence of soot as seen in Figure 9a. Adding ZDDP to the used oil reduces the effect of soot on the surface due to the formation of the tribofilm. As known that the ZDDP level increases in the oil, a higher rate of tribofilm growth is
expected and this could help to protect the surfaces from soot particles and improve the oil functionality. It is shown in Figure 9b that adding 0.75wt% ZDDP to the used oil reduces the effect of soot on surfaces significantly. There is still abrasive wear on the surface as soot overcomes the tribofilm formation and abrades on the surface as shown in Figure 9b. A higher rate of reforming tribofilm after being removed by soot occurred with a higher level of ZDDP (≥1.5wt% ZDDP). This can protect the surfaces from abrasive wear caused by soot as shown in Figure 9b, c and c1. It is observed that no abrasive wear was detected on surfaces with uneven distribution of tribofilm as shown in Figure 9c1. Adhesive wear on surfaces after adding ZDDP has been noted as shown in Figure 9c, c1. This could be due to the higher shear strength of ZDDP tribofilm between the rubbing surfaces causing adhesive wear23,47.
Figure 9: SEM surface analysis of wear scar on pins a) fresh oil a₁) used oil b) used oil+0.75wt% ZDDP b₁) used oil+1.5wt% ZDDP c) used oil+3wt% ZDDP c₁) used oil+5wt% ZDDP.

Microscope images confirm the distribution of tribofilm after adding ZDDP to the used oil compared to the fresh oil as shown in Figure 10. Where some regions are covered by tribofilm as shown in a dark area in wear scar, while other tribofilm regions are removed by soot. It is worth noting that ZDDP tribofilm attempts to protect the surfaces from soot particles, but soot abrades and removes the tribofilm from wear scar in some regions.

Figure 10: Microscope images of wear scar on pins after adding different levels of ZDDP.

### 3.3.4 Chemical composition of tribofilm

Energy Dispersive X-ray (EDX) analysis was conducted on the wear scar of pins to analyse the chemical composition of tribofilm. Chemical composition of the fresh oil sample at different positions demonstrates the uniform distribution of tribofilm as displayed in Figure 11a. EDX results revealed full removal of the whole tribofilm causing abrasive wear on the surface in the existence of soot as shown in Figure 9a₁. Adding ZDDP increased the concentration of three main elements S, Zn and P in the used oil as shown in Figure 6. Therefore, the concentration of these elements in the tribofilm composition is also increased compared to fresh oil as expected (Figure 11b at position 2). Tribofilm was not uniform on the surface after adding ZDDP (Figure 10) and this can be confirmed by chemical analysis of tribofilm at different positions. The results proved the distribution of tribofilm elements in wear scar after adding ZDDP and in the presence of soot is uneven (Figure 11b). The chemical composition of tribofilm reveals the coverage of the tribofilm at some regions and removal of tribofilm by soot at other regions. The results conclude that no full coverage of tribofilm after adding ZDDP even at a high level (5wt%) in the existence of soot particles.
| Elements | Position 1 (wt. %) | Position 2 (wt. %) |
|----------|-------------------|-------------------|
| Zn       | 1.09              | 0.95              |
| P        | 1.02              | 0.33              |
| S        | 0.77              | 1.25              |
| Ca       | 0.45              | 0                 |
| Fe       | 82.03             | 76.85             |
| C        | 6.94              | 16.05             |
| O        | 4.83              | 2.84              |
| Cr       | 1.52              | 1.16              |
| Si       | 0.23              | 0.14              |
| Mg       | 1.13              | 0.43              |
| Total    | 100               | 100               |

Figure 11: EDX chemical composition of tribofilm of wear scar on pins a) fresh oil b) used oil+5 wt%ZDDP samples at two positions.
3.4 ZDDP replenishment of reclaimed engine oil

3.4.1 Tribological performance

Used oil after removing soot performed higher wear compared to fresh oil due to the decomposition of antiwear additive and additive depletion as displayed in Figure 1 and Figure 5 respectively. Adding ZDDP at different levels to the reclaimed oil had a positive effect and decreased wear significantly as shown in Figure 12. As the ZDDP level increased in the oil, wear decreased gradually and performed better than fresh oil after adding 0.75wt% ZDDP. Replenishing the reclaimed oil with a level ≥0.75wt% ZDDP is sufficient to improve wear and extend the oil functionality. Post surface and tribofilm analysis will discuss if adding 0.75wt% ZDDP can provide fully tribofilm coverage after replenishing the depleted additive in the reclaimed oil.

Friction results as shown in Figure 12 reveal that the friction coefficient of reclaimed oil was less than the friction coefficient of fresh oil due to the presence of 0.26wt% soot. Existence of these particles in oils acted as a friction modifier between rubbing surfaces reducing the friction. However, it is good to mention that the existence of 0.26wt% soot did not affect wear value as shown in Figure 5. Friction increased with an increase in the amount of ZDDP in reclaimed oil as shown in Figure 12. Friction coefficient starts levelling with the amount of ≥3wt% ZDDP. The increase in friction coefficient after adding ZDDP to the reclaimed oil is due to the high roughing of tribofilm or the higher shear strength of tribofilm. The effect of the increase in ZDDP level on the coefficient of friction at the higher level is limited. The results are agreed with studies that demonstrated the effect of tribofilm on the friction coefficient can be stabilized at the high level of ZDDP.
3.4.2 Surface analysis

Figure 13 shows the wear scar of pins after replenishing the reclaimed oil at different levels of ZDDP compared to reclaimed and fresh oil samples. Abrasive wear was detected on the wear scar surface of reclaimed oil (Figure 13a) due to depletion and decomposition of additives. It was found that wear value reduced significantly after adding 0.75wt% ZDDP and performed better than fresh oil as shown in Figure 12. The surface of wear scar after adding 0.75wt% ZDDP showed no abrasive wear and full coverage of tribofilm as shown in Figure 13b. Additive replenishment at higher ZDDP percentage 1.5, 3 and 5wt% revealed no abrasive wear and uniform tribofilm formation as shown in Figure 13b, c, and c. Adhesive wear is observed after replenishing the reclaimed oil as displayed in Figure 13b, b, c, and c. This mostly comes from the higher shear strength of ZDDP tribofilm between the rubbing surfaces causing adhesive wear $^{23,47}$. 
Figure 13: SEM surface analysis of wear scar on pins a) fresh oil a,) reclaimed oil b) reclaimed oil+0.75wt% ZDDP b,) reclaimed oil+1.5wt% ZDDP c) reclaimed oil+3wt% ZDDP c,) reclaimed oil+5wt% ZDDP.

Microscope images as shown in Figure 14 display the distribution of tribofilm after adding ZDDP to the reclaimed oil compared to fresh oil. Where all regions on wear scar are protected by tribofilm represented as a dark area on wear scar. It is evident that no abrasive wear and full coverage of ZDDP tribofilm after replenishing the reclaimed oil.
EDX analysis of wear scar of pins after adding ZDDP at different levels to the reclaimed oil is presented in Figure 15. The results obtained from the chemical analysis of tribofilm of the reclaimed oil sample found no ZDDP tribofilm on the surface (Figure 15). The results of the chemical analysis of tribofilm after adding ZDDP to the reclaimed oil confirms the existence of tribofilm on the surface. The improvement in wear values after adding ZDDP (Figure 12) is reflected in the improvements in the chemistry of tribofilm. Presence of ZDDP in the reclaimed oil influences the chemical concentration of main tribofilm elements such as S, Zn and P. Figure 15 revealed that the higher level of ZDDP in the reclaimed oil was, the higher concentration of ZDDP elements was found in tribofilm. The tribofilm distribution on the surface after adding ZDDP to reclaimed oil was uniform as shown in Figure 16. Figure 16 demonstrates that the chemical analysis of tribofilm at different positions approximately has similar chemical concentrations of Zn, S and P. This leads to a conclusion that replenishing the reclaimed oil can improve the tribological performance and protect the surface by forming uniform tribofilm similar to the fresh oil.
Figure 15: EDX chemical composition of tribofilm of wear scar on pins after adding ZDDP to the reclaimed oil.

| Elements | Position 1 (wt.%) | Position 2 (wt.%) |
|----------|------------------|------------------|
| C        | 4.31             | 4.22             |
| O        | 2.54             | 2.71             |
| Si       | 0.23             | 0.19             |
| P        | 0.56             | 0.72             |
| S        | 0.23             | 0.2              |
| Ca       | 0.33             | 0.33             |
| Cr       | 1.52             | 1.68             |
| Fe       | 89.53            | 88.88            |
| Zn       | 0.74             | 1.07             |
| Total    | 100              | 100              |

Figure 16: EDX chemical composition of tribofilm on the pin for the reclaimed oil+0.75wt% ZDDP sample at two positions.
4. Conclusions

This study investigates the effect of ZDDP replenishment on the tribological performance in heavy-duty used oil. It was observed that the chemical structure of bulk oil did not change over use in the heavy-duty engine. While soot, antiwear decomposition and additive depletion were the main mechanisms that caused an increase in wear. ZDDP replenishment at different levels has been investigated for used oil containing soot and after removing soot. The main conclusions from this study can be summarised as follow:

- Wear decreases gradually with the reduction in soot percentage in the oil until 0.26wt% and then there was no change in wear value come from the soot.
- Chemical analysis of heavy-duty used oil using FTIR demonstrates no change in the chemical structure of the oil, but decomposition of antiwear additive occurred.
- The reduction in the elemental concentration of additives is due to additive depletion in the engine over use and additive adsorption on soot after being removed.
- Antiwear additives decomposition, additive depletion and additive adsorption on soot cause an increase in wear and abrasive wear on the surfaces.
- ZDDP replenishment process of used oil shows a higher level of ZDDP (3wt%) is required to improve wear value to be similar to fresh oil. Microscope and SEM images of wear scar reveal no abrasive wear on the surface after adding a high level of ZDDP. While EDX results show uneven distribution of tribofilm of surface in the existence of soot.
- ZDDP replenishment of the reclaimed oil demonstrates less amount of ZDDP (0.75wt%) is required to improve wear value to be similar to fresh oil.
- Surface analysis of reclaimed oil after adding 0.75wt% ZDDP shows uniform distribution of tribofilm and no abrasive wear was detected on the surface.

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6. Declaration of Interest Statement

There were no conflicts of interest.

7. References

1. Examiner P, Griffin WD. (12) United States Patent. 2010;2(12).
2. Nagai I, Endo H, Nakamura H, Yano H. Soot and valve train wear in passenger car diesel engines. SAE Int. 1983;92(Section 4: 831406–831830 (1983)):986-1000.
3. Motamen Salehi F, Morina A, Neville A. Zinc Dialkyldithiophosphate Additive Adsorption on Carbon Black Particles. Tribol Lett. 2018;66(3):0. doi:10.1007/s11249-018-1070-6

4. Berbezier I, Martin JM, Kapsa P. The role of carbon in lubricated mild wear. Tribol Int. 1986;19(3):115-122. doi:10.1016/0301-679X(86)90016-2

5. Colacicco P, Mazuyer D. The role of soot aggregation on the lubrication of diesel engines. Tribol Trans. 1995;38(4):959-965. doi:10.1080/10402009508983493

6. George S, Balla S, Gautam M. Effect of diesel soot contaminated oil on engine wear. 2007;262(September 2006):1113-1122. doi:10.1016/j.wear.2006.11.002

7. Green DA, Lewis R, Dwyer-Joyce RS. The Wear Effects and Mechanisms of Soot Contaminated Automotive Lubricants. 1996(May 2006). doi:10.1243/13506501JET140

8. Ramkumar P, Wang L, Harvey TJ, Wood RJK, Nelson K, Yamaguchi ES. The effect of diesel engine oil contamination on friction and wear. Word Tribol Congr. 2005;42010:537-538.

9. Green DA, Lewis R, Dwyer-Joyce RS. Wear effects and mechanisms of soot contaminated automotive lubricants. Proc Inst Mech Eng Part J Eng Tribol. 2006;220(3):159-169.

10. Sato H, Tokuoka N, Yamamoto H, Sasaki M. Study on wear mechanism by soot contaminated in engine oil (first report: relation between characteristics of used oil and wear). SAE Tech Pap. 1999;(0148-7191):9.

11. Nguele R, Al-salim HS, Mohammad K. Modeling and Forecasting of Depletion of Additives in Car Engine Oils Using Attenuated Total Reflectance Fast Transform Infrared Spectroscopy. 2014:206-222. doi:10.3390/lubricants2040206

12. Patty DJ, Lokollo RR. FTIR Spectrum Interpretation of Lubricants with Treatment of Variation Mileage. 2016;52:13-20.

13. Dörr N, Agocs A, Besser C, Ristić A, Frauscher M. Engine Oils in the Field : A Comprehensive Chemical Assessment of Engine Oil Degradation in a Passenger Car. Tribol Lett. 2019. doi:10.1007/s11249-019-1182-7

14. Al Sheikh Omar A, Motamen Salehi F, Farooq U, Morina A, Neville A. Chemical and physical assessment of engine oils degradation and additive depletion by soot. Tribol Int. 2021;160(April):107054. doi:10.1016/j.triboint.2021.107054

15. Green DA, Lewis R. The effects of soot-contaminated engine oil on wear and friction: A review. Proc Inst Mech Eng Part D J Automob Eng. 2008;222(9):1669-1689. doi:10.1243/09544070JAUTO468

16. Data PP. United States Patent ( 45 ) Date of Patent : 2008;2(12):1-4.

17. Kumar S, Mishra NM, Mukherjee PS. Additives depletion and engine oil condition - A case study. Ind Lubr Tribol. 2005;57(2):69-72. doi:10.1108/00368790510583375

18. Nguele R, Salim HS, Sasaki K. Oil Condition Monitoring Degradation Mechanisms and Additive Depletion. J Multidiscip Eng Sci Technol. 2015;2(3):355-360.

19. Kontou A, Southby M, Morgan N, Spikes HA. Influence of Dispersant and ZDDP on Soot Wear. Tribol Lett. 2018;66(4). doi:10.1007/s11249-018-1115-x

20. Lin YC, So H. Limitations on use of ZDDP as an antiwear additive in boundary lubrication. Tribol Int. 2004;37(1):25-33. doi:10.1016/S0301-679X(03)00111-7

21. Taylor LJ, Spikes HA. Friction-enhancing properties of zddp antiwear additive: Part i—friction
and morphology of ZDDP reaction films. Tribol Trans. 2003;46(3):303-309. doi:10.1080/10402000308982630

22. Yin Z, Kasrai M, Fuller M, Bancroft GM, Fyke K, Tan KH. Application of soft X-ray absorption spectroscopy in chemical characterization of antiwear films generated by ZDDP Part I: the effects of physical parameters. Wear. 1997;202(2):172-191.

23. Tomala A, Naveira-Suarez A, Gebeshuber IC, Pasaribu R. Effect of base oil polarity on micro and nanofriction behaviour of base oil + ZDDP solutions. Tribol - Mater Surfaces Interfaces. 2009;3(4):182-188. doi:10.1179/175158310X481709

24. Ghanbarzadeh A, Parsaeian P, Morina A, et al. A Semi-deterministic Wear Model Considering the Effect of Zinc Dialkyl Dithiophosphate Tribofilm. Tribol Lett. 2016;61(1):1-15. doi:10.1007/s11249-015-0629-8

25. Kano M, Yasuda Y, Ye JP. The effect of ZDDP and MoDTC additives in engine oil on the friction properties of DLC-coated and steel cam followers. Lubr Sci. 2004;17(1):95-103. doi:10.1002/ls.3010170108

26. Taylor LJ, Spikes HA. Friction-enhancing properties of ZDDP antiwear additive: Part i—friction and morphology of ZDDP reaction films. Tribol Trans. 2003;46(3):303-309. doi:10.1080/10402000308982630

27. Kontou A, Southby M, Morgan N, Spikes HA. Influence of Dispersant and ZDDP on Soot Wear. Tribol Lett. 2018;66(4):1-15. doi:10.1007/s11249-018-1115-x

28. Sniderman D. The chemistry and function of lubricant additives. Tribol Lubr Technol. 2017;73(11):18-28.

29. Gschwender LJ, Kramer DC, Lok BK. Liquid Lubricants and Lubrication. 2001.

30. DeJovine, James M. Homewood I. United States Patent (19). 1979;(19).

31. Lefebvre, Byron, Ft. Lauderdale F. Engine Oil Additive Dry Lubricant Powder. 1997;(19).

32. Raymond Rohde, Bartlesville O. Engine Oil Additive Dry Lubricant Powder. 1973;(19).

33. McCready DF. Engine Oil Additive Dry Lubricant Powder. 1983;(19).

34. Schneider E, St. Motors Corporation. Automatic Additive Replenishment System for IC Engine Lubricating Oil. 2005;2(12).

35. Wilk MA, Abraham WD, Dohner BR. An investigation into the effect of zinc dithiophosphate on ASTM sequence VIA fuel economy. SAE Tech Pap. 1996;105(1996):1310-1319. doi:10.4271/961914

36. ASTM Standards. Standard Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR). 2010;i. doi:10.1520/E2412-10.2

37. ASTM D7844-20. Standard Test Method for Condition Monitoring of Soot in In-Service Lubricants by Trend Analysis using Fourier Transform Infrared (FT-IR) Spectrometry. ASTM Int West Conshohocken, PA. 2020.

38. Bordg H, Desserprix G, Royet A, Stewart M. Soot Contamination in Engine Oil.

39. Truhan JJ, Qu J, Blau PJ. A rig test to measure friction and wear of heavy duty diesel engine piston rings and cylinder liners using realistic lubricants. Tribol Int. 2005;38(3):211-218.

40. Al Sheikh Omar A, Motamen Salehi F, Farooq U, Morina A, Neville A. Chemical and physical
assessment of engine oils degradation and additive depletion by soot. Tribol Int. 2021;160:107054. doi:https://doi.org/10.1016/j.triboint.2021.107054

41. Berbezier I, Martin JM, Kapsa P. The role of carbon in lubricated mild wear. Tribol Int. 1986;19(3):115-122.

42. Lubrecht AA, Venner CH, Colin F. Film thickness calculation in elasto-hydrodynamic lubricated line and elliptical contacts. Proc Inst Mech Eng Part J Eng Tribol. 2009;223(3):511-515.

43. Minami I. Applied Sciences Molecular Science of Lubricant Additives. 2017:445. doi:10.3390/app7050445

44. Salehi FM, Morina DNKA. Corrosive – Abrasive Wear Induced by Soot in Boundary Lubrication Regime. Tribol Lett. 2016;63(2):1-11. doi:10.1007/s11249-016-0704-9

45. Hu E, Hu X, Liu T, Fang L, Dearn KD, Xu H. The role of soot particles in the tribological behavior of engine lubricating oils. Wear. 2013;304(1-2):152-161. doi:10.1016/j.wear.2013.05.002

46. Taylor L, Dratva A, Spikes HA. Friction and wear behavior of zinc dialkyldithiophosphate additive. Tribol Trans. 2000;43(3):469-479. doi:10.1080/10402000008982366

47. Yang FW, Huang JM, Zhang GJ, et al. Tribological properties and action mechanism of a highly hydrolytically stable N-containing heterocyclic borate ester. Ind Lubr Tribol. 2016;68(5):569-576. doi:10.1108/ILT-06-2015-0074

48. Phillips OH, Lane PD, Shadday MC. Diesel engine wear with spin-on by-pass lube oil filters. SAE Tech Pap. 1979. doi:10.4271/790089

49. Loftis TS, Lanius MB. A new method for combination full-flow and bypass filtration: Venturi Combo. SAE Tech Pap. 1997. doi:10.4271/972957

50. Schwandt BW, Verdegan BM, Holm CE, Fallon SL, Khosropour MM. Cleanable heavy duty oil filters for trucks and buses. SAE Tech Pap. 1996;105(May):2439-2447. doi:10.4271/962240

51. Galsworthy J, Hammond S, Hone D. Oil-soluble colloidal additives. Curr Opin Colloid Interface Sci. 2000;5(5-6):274-279. doi:10.1016/S1359-0294(00)00066-2

52. Motamen Salehi F, Morina A, Neville A. Zinc Dialkyldithiophosphate Additive Adsorption on Carbon Black Particles. Tribol Lett. 2018;66(3):0. doi:10.1007/s11249-018-1070-6