

# The Influence of Zinc-Dialkyl-Dithiophosphate (ZDDP) Additives on the Tribological Performance of RBD Palm Kernel

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## ABSTRACT

*Vegetable oil based lubricant has received much attention in recent years due to its biodegradable properties, low toxicity and environmental friendly. This study used refined, bleached and deodorized (RBD) palm kernel blended with zinc-dialkyl-dithiophosphate (ZDDP) to evaluate the tribological performance as a potential alternative lubricant. The ZDDP additives were added with concentration of 0wt%, 1wt%, 3wt% and 5wt%. Commercial mineral oil SAE 40 was used for comparison purposes. The tests were performed at 1.5 m/s and 3.5 m/s of sliding speed under 9.81 applied load for 1 hour at room temperature. The results indicate that the presence of ZDDP in RBD palm kernel have improved both friction reducing and anti-wear performance. The formulation of RBD palm kernel have the potential to be used as a substitution for mineral based lubricant in near future. The authors would like to express their thanks to the Research Management Centre*

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**Keywords:** *ZDDP, Coefficient of Friction (COF), Wear Coefficient*

## Introduction

Mineral based lubricant is extensively used in various applications due to its overall performance. This lubricant is come from non-renewable resources which is very high toxic and not readily biodegradable, thereby will cause environmental problem. Much research in recent years has focused on vegetable oils due to its biodegradable properties and environmental friendly characteristics, which offer important economic benefits. Palm oil come from renewable resources that possess high biodegradability, low toxicity and definitely will not be harmful to the environment.

A number of previous studies have investigated the tribological performance of palm oil as based lubricant. Masjuki et al. [1] found that palm oil based lubricant exhibited better anti-wear performance while mineral oils based lubricant exhibited better friction performance. Ing et al. [2] demonstrated contradicted finding, which they found RBD palm olein has lower coefficient of friction compared to paraffinic mineral oil but create larger wear scar. Some researchers have attempt to assess the tribological characteristics of palm oil as an additive in mineral based lubricant. Zulkifli et al. [3] observed 3% addition of palm oil-based TMP (trimethylolpropane) ester in ordinary lubricant have the best anti-wear and anti-friction properties. More work are needed to improve the lubricant performance to meet industry requirement because proper lubrication is critical in all machinery components to reduce friction and wear, maximize efficiency and extend machine life [4].

Fatty acid compositions in vegetable oils make them susceptible to oxidation and thermal degradation [5][6]. Previous studies have focused on improving these limitations by making chemical modifications [7] and genetic modifications [8] to existing vegetable oils. An alternative method to improve the tribological performance of vegetable oils is by adding functional additive packages into the vegetable oils where it is found to be more cost effective and most efficient solution. Zinc-dialkyl-dithiophosphate (ZDDP) have long been recognized to be effective anti-wear additives and used for improving oxidative stability of the commercially available lubricants [9]. The effectiveness of additive depends on their structure and

concentration, applied load, sliding speed, contact temperature, time of interaction, and surface materials [10].

Work done by Cheenkachorn [11] discovered that the addition of 1% ZDDP in soybean oil, epoxidized soybean oil and high oleic soybean oil reduces the coefficient of friction significantly especially for lower temperature. It is thought that the desorption rate of additive on the surface is higher than the adsorption rate at higher temperature. The addition of additive effectively protected the rubbing surfaces since it can form a protective thin film by attaching a polar head to the metal and the non-polar ends can form a molecular layer. Jayadas et.al. [12] investigated the tribological properties of pure coconut oil and ZDDP additive added in coconut oil. The results were compared with commercial mineral oil SAE20W50. Their analysis revealed that wear scar diameter of pure coconut oil was higher than SAE 20W50 although the friction coefficient (COF) of coconut oil is much smaller. But, when 2wt% of ZDDP additive added into the coconut oil it has improved both anti-friction and anti-wear performance.

The present paper presents the influence of additive concentration on the friction and wear performance of refined, bleached and deodorized (RBD) palm kernel by using pin-on-disk tribotester. Experimental results show that the presence of ZDDP in RBD palm kernel have reduced the coefficient of friction and wear scar diameter. Using an optical microscope, we observe an abrasive wear as a dominant wear occur on the pins specimen and the rougher surface roughness of the worn surface of the pins correspond to the deeper of groove.

## **Materials and Methods**

### **Lubricants and Additives**

Commercial ZDDP was mixed with RBD palm kernel at weight (%) concentrations of 0%, 1%, 3% and 5% to study the influence of additive concentration on tribological performance. Commercial mineral oil (SAE 40) was used for comparison purposes. The mixture of RBD palm kernel and ZDDP were prepared using a stirrer for an hour and the temperature of the blended lubricants were kept in between 40°C to 50°C.

### **Experimental Procedure**

These experiment were carried out to evaluate the tribological performance of additive/RBD palm kernel mixtures using pin-on-disk tribotester. The pin and disk were cleaned with acetone before each test to ensure there is no any debris on the surfaces. The pins used in the tests were 6 mm diameter and made of A1100 pure aluminium with a composition of Si, 0.08%; Fe, 0.33%; Mg, 0.0016%; Cu, 0.054%; Ti, 0.013%; Zn, 0.013% and Al, 99% (min) and a hardness of HV 30. While the disk were in 160 mm diameter and made of

SKD11 stainless steel with a composition of C, 1.55%; Si, 0.30%; Mn, 0.35%; Cr, 11.75%; Mo, 0.75%; V, 0.95%; S, 0.005% and P, 0.02% [13].

The wear disk was mounted on the disk holder and fixed with four screws. The pin was held by the pin holder and it should touch the wear disc top. The stationary pin was in contact with the disk at a constant vertical force while the disk was rotated at a specified speed, creating a sliding contact. The load was then applied at one end of the lever and act as counterweight to balance the pins. The contact point of the pin and rotating disk was lubricated under a limited amount of lubricant (2.5 ml). So, the disk was designed to have a groove in order to ensure the tested lubricants did not flow out during the rotation of disk. The frictional force sensor or load cell measures the friction torque between stationary pin and rotating disk, which were then used to calculate the coefficient of friction (COF). These experiments were performed at two different sliding speeds of 1.5 m/s and 3.5 m/s. All the tests were carried out at applied loads of 9.81 N. Temperature for all the tests was at room temperature and the tests were conducted for 1 hour.

### **Surface Analysis**

A surface profiler was used to measure the surface roughness of the worn surface of the pins. The measured surface roughness was an arithmetic mean surface roughness (Ra) and reported in unit micrometer ( $\mu\text{m}$ ). Prior to the analysis, the pins were cleaned by acetone in order to eliminate the residual lubricant. Then, the physical appearance of the pins' worn surface was observed with an optical microscope at the magnification of 200 $\mu$ .

## **Results and Discussion**

### **Viscosity Analysis**

Viscosity is the most important criterion in a selection of oil and defined as the measure of resistance to flow. It refers to the thickness of the oil to keep the minimum friction and prevent wear from occurring when two sliding surfaces are in contact. High viscosity refers to high resistance to flow and low viscosity refers to low resistance to flow. The viscosity index (VI) indicates changes in viscosity with changes in temperature and it is also an important indicator for selecting a lubricant. In the present study, the viscosity of the tested lubricants were determined by a rotary viscometer as per ASTM 2983 and its viscosity index (VI) were obtained in accordance to ASTM D2270.

Figure 1 shows the kinematic viscosity of RBD palm kernel blended with ZDDP additive and its viscosity index (VI). The viscosity was determined by viscometer at 40°C and 100°C. PK possess higher VI or smaller change in viscosity with temperature compared to SAE 40 due to the presence of triglyceride structure in PK that can maintain stronger

intermolecular interactions with increasing temperature than branched hydrocarbons in SAE 40 [14]. Furthermore, the results indicate the viscosity of RBD palm kernel (PK) blended with 1wt% ZDDP have higher kinematic viscosity at 40°C but it shows the lowest at 100°C. Among these blended lubricants, PK+1% ZDDP shows low viscosity index (VI) which indicates significant changes in viscosity as the temperature increases. This means that PK+1% ZDDP has unstable thin film forming ability at higher temperature.

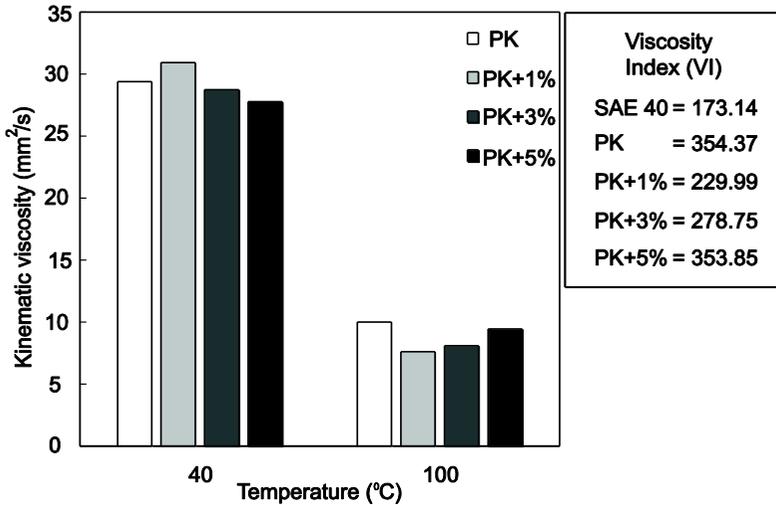


Figure 1: Kinematic viscosity of ZDDP/RBD palm kernel (PK) mixtures at 40°C and 100°C.

### Friction Reducing Performance

The coefficient of friction (COF) of RBD palm kernel with various ZDDP additive concentrations at 1.5 m/s and 3.5 m/s of sliding speed are illustrated in Figure 2. It is seen that at 1.5 m/s COF of PK is higher than that of benchmark lubricant SAE 40, then COF are reduced with an increased in ZDDP additive concentrations. While at higher speed (3.5 m/s), PK seem to have smaller COF than SAE 40 where the COF values are at 0.085 and 0.099 respectively. COF of SAE 40 was lower than that of PK at 1.5 m/s sliding speed attributed by the presence of free fatty acids in the SAE 40 that used as ‘friction modifiers’ in mineral oils under boundary lubrication conditions. These free fatty acids will interact with the steel surface to produce a more effective lubricant layer than vegetable oils alone [8]. While PK shows better friction reducing abilities than SAE 40 under high sliding speed due to the presence of unsaturated fatty acid content in PK that enable them to produce

an effective lubricant layer or soap film on the metal surface by the chemical adsorption to prevent direct metal-to-metal contact, hence reduced the friction [15].

At both sliding speeds, PK+5wt% ZDDP demonstrate as the best friction reduction performance. Compared with pure RBD palm kernel, addition of 5wt% in RBD palm kernel have reduced approximately at 50.8% and 45.9% in COF at 1.5 m/s and 3.5 m/s respectively. It is evident that the ZDDP was responsible for the protection of the RBD palm kernel against oxidation. ZDDP has long been recognized for its ability as antioxidant to resist oxidation degradation. ZDDP functions both as radical scavenger and peroxide decomposer [16]. The presence of organic molecules such as zinc, phosphorus and sulphur in ZDDP making them as a powerful antioxidant since those organic molecules are bound to the metal surface to form a protective coating on the metal surface. The sulphur and phosphorus compounds also will react with metal surface to forms a low shear strength film, thus reducing COF [17].

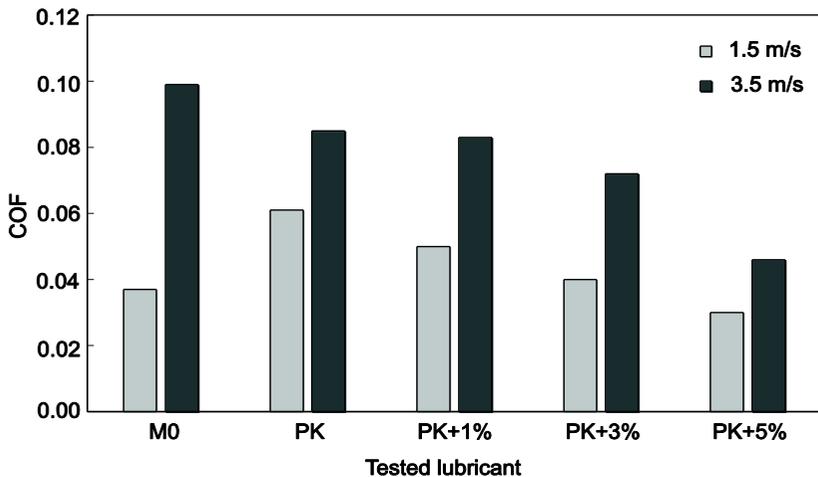


Figure 2: Coefficient of friction (COF) of the pin specimen at 1.5 m/s and 3.5 m/s.

### Anti-wear Performance

Figure 3 gives the wear scar diameter (WSD) of the pin specimen lubricated with SAE 40, PK, PK+1wt%ZDDP, PK+3wt% ZDDP and PK+5wt% ZDDP at the sliding speed of 1.5 m/s and 3.5 m/s. The amount of the wear on pin also can be expressed in wear coefficient where it was determined based on the measurement of WSD. The wear coefficient was calculated using

Archad's law as shown in Equation (1) in order to characterize tribological response of pin and disk contacts. All the calculated data were tabulated in Table 1. Smaller WSD and wear coefficient demonstrate the superior wear resistance of the lubricant.

$$K = \frac{VH}{SF} \quad (1)$$

where K is the dimensionless wear coefficient, V is the volume of material removed by wear, H is the hardness of the specimen, S is the sliding distance and F is the applied force [18].

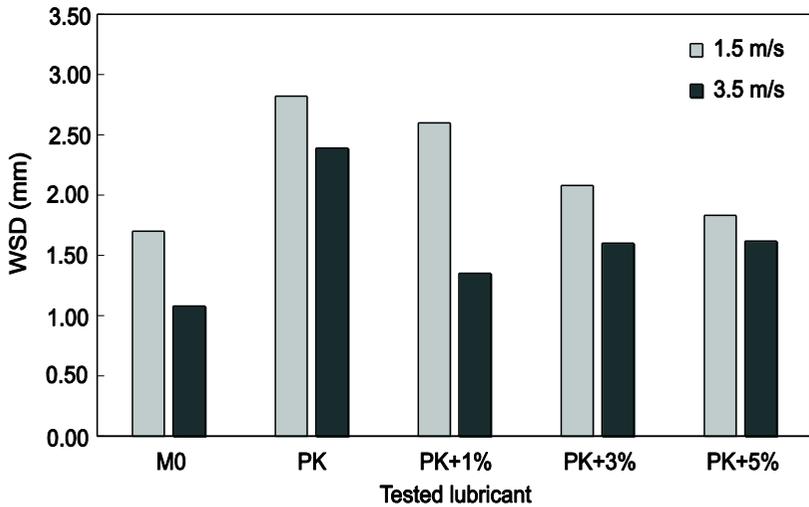


Figure 3: Wear scar diameter (WSD) of the pins specimen at 1.5 m/s and 3.5 m/s.

Table 1: Pin wear volume and wear coefficient of pins specimen at 1.5 m/s and 3.5 m/s.

Sliding speed (m/s)	Lubricant	Pin wear volume (mm <sup>3</sup> )	Wear coefficient
1.5	SAE 40	0.137	7.74 x 10 <sup>-5</sup>
	PK	1.035	5.86 x 10 <sup>-4</sup>
	PK+1% ZDDP	0.748	4.23 x 10 <sup>-4</sup>
	PK+3% ZDDP	0.306	1.73 x 10 <sup>-4</sup>
	PK+5% ZDDP	0.184	1.04 x 10 <sup>-4</sup>

3.5	SAE 40	0.022	$5.40 \times 10^{-6}$
	PK	0.534	$1.30 \times 10^{-4}$
	PK+1% ZDDP	0.054	$1.32 \times 10^{-5}$
	PK+3% ZDDP	0.107	$2.60 \times 10^{-5}$
	PK+5% ZDDP	0.113	$2.74 \times 10^{-5}$

Generally, it can be seen that PK generate larger WSD and wear coefficient than that of SAE 40. Although PK have lower COF than SAE 40 at 3.5 m/s of sliding speed, it generates larger WSD. The data obtained also is in good agreement with a statement by Ing et al. [19] which stated that vegetable oils that having low COF does not mean it also have low wear rate. They indicated that vegetable oil possess high wear rate due to the present of fatty acid that can chemically reacted with the metal surface during sliding. The effective lubricant layer on the metal surfaces that form earlier will rubs away and produces nonreactive detergents, thereby increase wear. The decreased in WSD and wear coefficient of PK when blended with ZDDP additive can be contributed to the formation of protective film on the metal surface. ZDDP effectively reduce wear when the sulphur and phosphorus elements acting on the metal surfaces to form polymer-like layer when the sliding contact occurs [20]. This protective film also will remove any peroxy-radicals caused by oxidation and disintegrated any wear debris on the metal surface, thereby reducing the wear.

On the other hand, at 3.5 m/s sliding speed it is found that 1wt% of ZDDP is an optimum concentration in reducing WSD and wear coefficient of PK but it showed a slight increase with the addition of ZDDP above 3wt%. At high speed, the lubricant layer highly depend on the viscosity of the lubricant because high speed will cause more metal-to-metal contact through the breakdown of the protective film, thereby increase in wear. PK+1wt% ZDDP had the highest viscosity compared with non-additive added PK and other additive added concentration. It is the plausible reason PK with 1wt% ZDDP had lower WSD, where it is able to prevent metal-to-metal contact by providing the adequate protective lubricant film on the metal surface.

### Surface Analysis

Arithmetic mean surface roughness parameter (Ra) was measured in a perpendicular direction to the sliding using a surface profiler. The surface roughness value is related to the scratch formation or abrasive groove on the pin surface, where deeper scratches will produce a coarser surface roughness. The abrasive groove represents the material loss caused by the formation of wear debris during sliding. The surface roughness values were plotted in Figure 4 and it was observed that PK generated a coarser surface roughness than SAE 40 at both 1.5 m/s and 3.5 m/s where the difference were approximately 28.9% and 45.8% respectively. The PK generated a coarser

surface roughness due to the removal of the soap film by the continuous rubbing of the contact surfaces. The destruction of this soap film caused greater metal-to-metal contact and generated deeper scratches on the pin surface. This phenomenon is related to the oxidation process that occurs on metal surfaces since the unsaturated fatty acid in the PK and PS easily absorbs oxygen and hence, affects the reactions within the lubricant [15].

The addition of ZDDP additive in PK have a positive effect on the surface protection where it produced smoother surface with an increase in ZDDP concentration. Figure 4 shows that the PK with 5wt% ZDDP additive showed a comparatively smooth surface roughness compared to the other tested lubricants at both sliding speed conditions. The presence of ZDDP in the PK contributed to the prevention of rapid oxidation, hence minimizing the rate of removal of the soap film, resulting in a smoother surface.

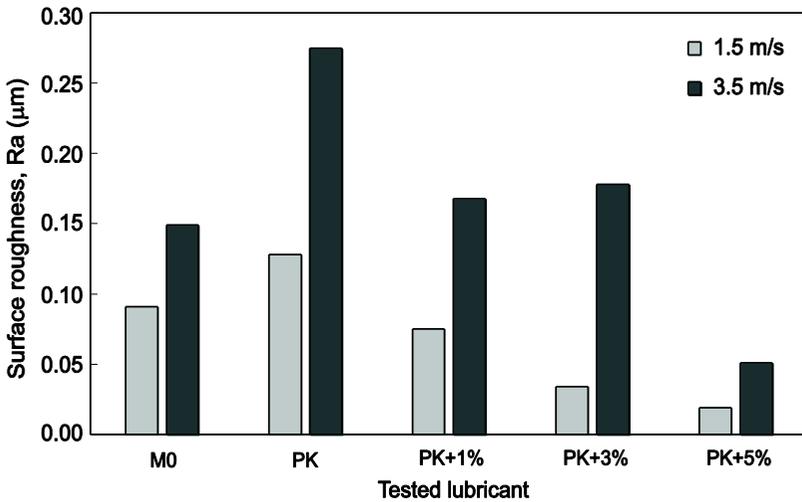


Figure 4: Surface roughness (Ra) of the pins specimen at 1.5 m/s and 3.5 m/s.

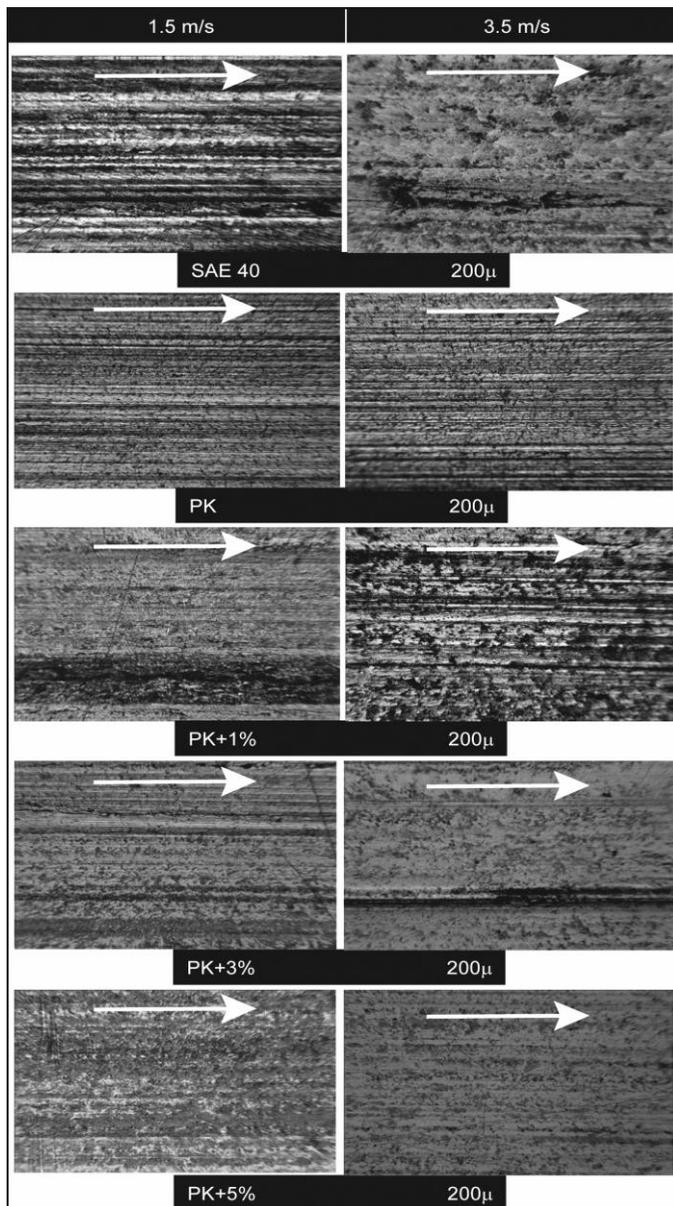


Figure 5: Physical appearance of the pin's worn surface at 1.5 m/s and 3.5 m/s.

Further analysis on the wear worn surface of the pin using high resolution optical microscope. The physical appearance of the pin's worn surfaces lubricated by SAE 40, PK, PK+1wt% ZDDP, PK+3wt% ZDDP and PK+5wt% ZDDP at sliding speed of 1.5 m/s and 3.5 m/s were shown in Figure 5. Generally, abrasive wear represents by the parallel groove formed on the pin's worn surfaces of all tested lubricants. It was found that PK generated deeper scratches on the worn surfaces caused by the breakdown of the lubricant film, which was probably due to the occurrence of oxidation on the metal surfaces. Oxidation occurs on the metal surfaces will caused more material removal. The presence of ZDDP acting as an antioxidant agents in PK that can resist the oxidation on the metal surface, thereby prevent from more material removal. It was observed that 5wt% ZDDP in PK generate smoother worn surface due to the formation of protective lubricant film on the metal surface.

## **Conclusion**

The influence of ZDDP additives on the tribological performance of RBD palm kernel was evaluated using pin-on-disk tribotester. The ZDDP additive blended with RBD palm kernel in a mixture of 0wt%, 1wt%, 3wt% and 5wt%. The experiment were conducted at two sliding speeds of 1.5 m/s and 3.5 m/s under 9.81 applied load for 1 hour testing time. Commercial mineral oil SAE 40 was used for comparison purposes. The results showed that unformulated RBD palm kernel had higher coefficient of friction (COF) and wear scar diameter (WSD) compared to SAE 40 at 1.5 m/s of sliding speed. Whereas it had lower COF than SAE 40 at 3.5 m/s of sliding speed, but create larger WSD. The presence of ZDDP additives in RBD palm kernel have improved both friction reducing and anti-wear performance. From the observation of the surface morphologies of the worn surfaces, ZDDP effectively protect the pin surface from wear. It can be concluded that the formulation of RBD palm kernel have the potential to be used as a substitution for mineral based lubricant in near future.

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