

# Tribological Behaviour of Zinc Dialkyl-Dithiophosphate (ZDDP) as a Lubricant Additive in RBD Palm Stearin

A.N. Farhanah<sup>\*,a</sup>, and S. Syahrullail<sup>b</sup>

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia. <sup>a.\*</sup>nurulfarhanahazman@gmail.com, <sup>b</sup>syahruls@mail.fkm.utm.my

**Abstract** – The effects of ZDDP additive concentrations in refined, bleached and deodorized (RBD) palm stearin on the tribological behaviour were tested. Pure RBD palm stearin and additive added with concentration of 0%, 1%, 3% and 5% (in weightage) were used in pin-on-disk triboteter (ASTM G99). Tests were performed under 3.5 m/s sliding speed and 9.81 N force applied on the pin. Each test was run in an hour at room temperature. Friction and wear performance of pure RBD palm stearin and ZDDP-added were compared. The results show that the presence of ZDDP additive in RBD palm stearin improved both friction and wear performance. ZDDP additive also can effectively act as antioxidant agent in RBD palm stearin. **Copyright © 2015 Penerbit Akademia Baru - All rights reserved.** 

Keywords: ZDDP, Friction, Wear, Roughness, Oxidation

## **1.0 INTRODUCTION**

Friction and wear are the main factors that can shorten machines and engines life, consequently it will give impact on economic. This problem can be overcome with the presence of lubricant since the main function of lubricant is to reduce friction and wear between two moving surfaces. It was estimated billions of dollars per year could be save if the life of machines and engines could be extended since it can reduce their maintenance cost and operation time [1]. In 2004, approximately 37.4 million tonnes of lubricants were consumed worldwide. Automotive lubricants accounts for the largest amount at nearly 53 percent of the total lubricants market, followed by industrial lubricants (32%), process oil (10%) and marine oils (5%) [2]. The growing of automotive and industrial sectors have resulted in enhanced demand for lubricants. The lubricant used are mainly from mineral based lubricant due to its overall performance.

However, due to environment damage caused by mineral oil, industry start developing lubricant from vegetable oil. Vegetable oil are selected due to its environmental friendly, biodegradable and non-toxic [3]. Many previous research have been reported for various types of vegetable oils like coconut oil [4], Jatropha oil [5], rapeseed oil [6], canola oil [7], safflower oil, cottonseed oil, soybean oil, sunflower oil [8] and palm oil [9-13]. Palm oil are becoming more attractive in a wide range of application and have a great potential for lubrication. Recently, numerous research have been conducted using palm oil as lubricant in various

applications, including biodiesel [9], industrial-cutting lubricants [10], metal-forming process [11], hydraulic fluids [12] and as a source of lubrication in the biomedical industry [13]. So, palm oil was specifically chosen in this present study because of its availability and inexpensive.

Previous findings have displayed the potential for lubricant formulated from vegetable oils in a wide range area. However, vegetable oils are limited in oxidative stability and thermal stability [14] include cloudiness, precipitation, poor flow ability and solidification at relatively high temperatures [15]. These properties can be improved by the addition of suitable additives such as sulphur-phosphorus compounds, organo-zinc compounds and aromatic amine compounds for improving oxidative stability and polymethacrylates for improving thermal stability [16]. Present study have selected zinc dialkyl-dithiophosphate (ZDDP) additive as it is already known as good antiwear and antioxidant agents [17].

The purpose of this study was to examine the effect of ZDDP additive concentrations on the tribological properties of RBD palm stearin. RBD palm stearin formulated with 0%, 1%, 3% and 5% (in weight) ZDDP were prepared and evaluated on a pin-on-disk tribotester. The results were compared with commercial mineral oil SAE 40. It is concluded that incremental of ZDDP additive concentration showed substantial improvement in both coefficient of friction and wear scar diameter.

## 2.0 METHODOLOGY

#### 2.1 Materials and Lubricants

The pin used in this research was made up from pure aluminum A1100 with density of 2.71 g/cm3. While the disk was from tool steel SKD11 with density of 7.85 g/cm3. In the present study, refined, bleached and deodorized (RBD) palm stearin was tested with regard to its friction and wear behaviour. The effect of ZDDP additive's concentrations on its tribological behaviour also tested. A well-blended of 1wt%, 3wt% and 5wt% ZDDP in RBD palm stearin were achieved using a stirrer with additional heat.

Lubricant	<b>RBD Palm Stearin</b>	<b>SAE 40</b>
Specific density (g/cm <sup>3</sup> )	0.88	0.86
Dynamic viscosity at 40°C (mPas)	38.01	114.0
Dynamic viscosity at 100°C (mPas)	8.55	17.8

Table 1: General properties of tested lubricant

#### 2.2 Pin-on-disk Tribotester

A pin-on-disk tribotester was used in this experiment to evaluate the tribological performance of the tested lubricants (see Figure 1). 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 test conditions applied in this experiment were shown in Table 1. Wear scar diameter of the pins also were measured to calculate the pin volume loss. The pin volume loss was calculated as in Equation (1) [8].

$$V = \frac{\pi r^4}{4R} \tag{1}$$



where r is radius of pin wear scar (in unit mm) and R is original pin radius (in unit mm)

Parameter	Conditions
Pin	A1100, $Ø = 6 \text{ mm}$
Disk	SKD11, Ø = 160 mm
Load	9.81 N
Sliding speed	3.5 m/s
Temperature	Room temperature





Figure 1: Pin-on-disk tribotester

#### 2.3 Surface Analysis

At the end of the experiment, surface roughness of the pins was measured perpendicular to the direction of sliding by a surface profiler. Surface roughness parameter, Ra was used to describe the surface features of the wear components. In addition, surface topography of the slider profile also were taken to correlate it with Ra value. Metallurgy of the pin's surface were analysed after each test and it was measured using an optical microscope. The pins were cleaned by using acetone to ensure there was no excess oil on the pin's surface.

#### 3.0 RESULTS AND DISCUSSION

#### 3.1 Friction and Wear Analysis

Coefficient of friction and wear scar diameter of SAE 40, RBD palm stearin (PS) and PS+5wt% ZDDP determined as per ASTM G99 were as shown in Table 2. RBD palm stearin have higher COF and WSD compared with SAE 40. Addition of ZDDP in 5% (in weightage) have substantial improvement in both COF and WSD of RBD palm stearin as indicated in Table 2. ZDDP additive contains aggressive non-metal (sulphur and phosphorus) that react with exposed metallic surfaces creating protective, low-shear-strength surface films that reduce friction and wear [18].



Friction and wear behaviour of RBD palm stearin with various additive concentrations were evaluated using pin-on-disk tribotester. The coefficient of friction (COF) of RBD palm stearin with various ZDDP additive concentrations are illustrated in Figure 2. Incremental in ZDDP additive concentrations reduced COF where PS+5wt% ZDDP demonstrate as the best friction reduction performance. Compared with pure RBD palm stearin, addition of 5wt% in RBD palm stearin have reduced more than 75% reduction in COF. At any percentage of ZDDP concentration in RBD palm stearin, the COF obtained were lower than pure RBD palm stearin. It is concluded that ZDDP additive absorb effectively on the metal surfaces and form a thin film. The thin film between the mating surfaces will prevent metal contact hence reduce COF.

Figure 3 illustrated the antiwear performance of RBD palm stearin with various concentrations of ZDDP. Smaller WSD demonstrate the superior wear resistance of the lubricant where WSD was measured after each test using an optical microscope. WSD of the pins were effectively reduced with the presence of ZDDP additive in the RBD palm stearin; increased in ZDDP concentrations reduced WSD significantly. PS+5wt% ZDDP delivered the best antiwear performance which more than 50% reduction in WSD was observed when compared with pure RBD palm stearin. The amount of the wear on pin also can be expressed in volume loss where it was determined based on the measurement of WSD. Volume loss of the pins were calculated as in Equation (1) and tabulated in Table 3. As seen in Figure 3 and Table 3, the WSD and pin volume loss of ZDDP-added RBD palm stearin were lower than pure RBD palm stearin. Lin and So [19] reported that the anti-wear performance of ZDDP results from physisorbed film that prevent from metal-to-metal contact at low temperatures. Choi et al. [20], however, claimed that the anti-wear capability of anti-wear (AW) additives depended on the shear strength of the protective film formed.

**Table 3:** Coefficient of friction (COF) and wear scar diameter (WSD) of SAE 40, RBD palmstearin (PS) and PS+5wt% ZDDP determined as per ASTM G99

Lubricants	COF	WSD (mm)	
PS	0.153	4.05	
SAE 40	0.099	1.08	
PS+5wt%ZDDP	0.036	1.86	



Figure 2: Effect of ZDDP concentrations on COF





Figure 3: Effect of ZDDP concentrations on WSD

Table 3: Volume loss of the pins of RBD palm stearin with various ZDDP concentrations

Lubricants	PS	PS+1%	PS+3%	PS+5%
Volume loss (mm <sup>3</sup> )	4.403	2.841	1.173	0.196

#### **3.2 Surface Analysis**

Slider profile of the pins and their surface roughness parameter, Ra are shown in Figure 4. As can be seen, the pin's surface becomes smoother as the concentration of ZDDP additive increased. This means that the presence of ZDDP additive in RBD palm stearin can effectively protect the surface from being rub away during sliding contact occur. A thin lubricant film was formed to protect the surface hence reduced wear and create smooth surface. In addition, the roughness of the pin's surface have a direct relationship with COF. The pins that were run in pure RBD palm stearin have the rougher surface as well as high COF. The slider profile corroborates the COF, where steeper peak means there are more material removal and more abrasive groove on the pin's surface.





# **Figure 4:** Slider profile and surface roughness parameter (Ra) of the tested pins after each test; (a) RBD palm stearin (PS), (b) PS + 1wt% ZDDP, (c) PS + 3wt% ZDDP and (d) PS + 5wt% ZDDP

Figure 5 shows the morphologies of the wear worn surface assessed using an optical microscope. The arrows on the figure show their sliding directions. Generally, abrasive wear was the dominant wear mechanism found in Figure 5 since there are some parallel grooves on the worn surface. The antiwear performance can be associated with surface roughness and the surface morphologies of the pins. From these figure, a deep and abrasive groove is observed in the pure RBD palm stearin. These grooves increased both surface roughness and COF. Some darker regions also can be seen on the wear surfaces of the pin. The darker region represents oxidation occur on the pin surface. Oxygen will oxidized on the metal surface and weakened the metal surface [21]. Oxidation occur due to the rapid reactions of unsaturated double bonds in the fatty acids and strong intermolecular reactions to form a thin film [22]. Comparing the effect of ZDDP additive in Figure 5, it was observed that increase in ZDDP concentration has a significant improvement in wear performance in reduction of abrasive wear and oxidation.



**Figure 5:** Wear worn surface of the tested pins; (a) RBD palm stearin (PS), (b) PS + 1wt% ZDDP, (c) PS + 3wt% ZDDP and (d) PS + 5wt% ZDDP

#### **4.0 CONCLUSSION**

From this experiments, it can be concluded that ZDDP additive can be used as additive in RBD palm stearin. In this study, the effect of ZDDP concentrations was investigated using pin-on-disk tribotester.

- It was found that the addition of ZDDP additive into RBD palm stearin resulted in reduction of COF and WSD
- Surface roughness parameter, Ra have a direct correlation with COF; high COF generate rougher surfaces
- Abrasive wear was the dominant wear mechanism occur on the tested pins' surface; pure RBD palm stearin have more parallel groove and a darker region exist on the pin surface
- ZDDP additive in RBD palm stearin effectively act as antiwear and antioxidant agents in RBD palm stearin.

#### ACKNOWLEDGEMENT



The authors would like to express their gratitude to the Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM) for their support and cooperation during this study. The authors also thanked Research Management Centre (RMC), UTM for the Research University Grant (02G34, 02G35, 09H64) and Fundamental Research Grant Scheme (4F610) for their financial support.

#### REFERENCES

- N. Sapawe, S. Syahrullail, M. I. Izhan. Evaluation on the tribological properties of palm olein in different loads applied using pin-on-disk tribotester, Jurnal Tribologi 3 (2014) 11–29.
- [2] P. Nagendramma, S. Kaul. Development of ecofriendly/biodegradable lubricants: An overview, Renewable and Sustainable Energy Reviews 16 (1) (2012) 764–774.
- [3] M. Shahabuddin, H. H. Masjuki, M. a. Kalam, M. M. K. Bhuiya, H. Mehat. Comparative tribological investigation of bio-lubricant formulated from a non-edible oil source (Jatropha oil), Industrial Crops and Products 47 (2013) 323–330.
- [4] N. H. Jayadas, K. Prabhakaran Nair, A. G. Tribological evaluation of coconut oil as an environment-friendly lubricant, Tribology International 40 (2007) 350–354.
- [5] I. Golshokouh, M. Golshokouh, F. N. Ani, E. Kianpour, S. Syahrullail. Investigation of physical properties for jatropha oil in different temperature as lubricant oil, Life Science Journal 10 (2013) 110–119.
- [6] S. Arumugam, G. Sriram. Synthesis and characterisation of rapeseed oil bio-lubricant its effect on wear and frictional behaviour of piston ring-cylinder liner combination, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 227 (2012) 3–15.
- [7] H. Duzcukoglu, Ö. S. Şahin. Investigation of wear performance of canola oil containing boric acid under boundary friction condition, Tribology Transactions 54 (2010) 57–61.
- [8] H. Oğuz, H. Düzcükoğlu, Ş. Ekinci. The investigation of lubrication properties performance of euro-diesel and biodiesel, Tribology Transactions 54 (2011) 449–456.
- [9] A.S.M.A Haseeb, S.Y. Sia, M.A. Fazal, H.H. Masjuki. Effect of temperature on tribological properties of palm biodiesel, Energy 35 (2010) 1460–1464.
- [10] E.A. Rahim, H. Sasahara. Investigation of tool wear and surface integrity on MQL machining of Ti-6AL-4V using biodegradable oil, Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacturing 225 (2011) 1505– 1511.
- [11] S. Syahrullail, C.S.N. Azwadi, M.R. Abdul Kadir, N.E.A. Shafie. The effect of tool surface roughness in cold work extrusion, Journal of Applied Science 11 (2011) 367– 372.



- [12] W.B. Wan Nik, M.A. Maleque, F.N. Ani, H.H. Masjuki. Experimental investigation on system performance using palm oil as hydraulic fluid, Industrial Lubrication and Tribology 59 (2007) 200–208.
- [13] D.M. Razak, S. Syahrullail, N. Sapawe, Y. Azli, N. Nuraliza. A New approach using palm olein, palm kernel oil, and palm fatty acid distillate as alternative biolubricants: improving tribology in metal-on-metal contact, Tribology Transactions 58 (2015) 511– 517.
- [14] N.J. Fox, B. Tyrer, G.W. Stachowiak. Boundary lubrication performance of free fatty acids in sunflower oil, Tribology Letters 16 (2004) 275–281.
- [15] H. Hwang, S.Z. Erhan. Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point, Journal of the American Oil Chemists' Society 78 (2001) 1179–1184.
- [16] A. Aravind, M.L. Joy, K.P. Nair. Lubricant properties of biodegradable rubber tree seed (Hevea brasiliensis Muell. Arg) oil, Industrial Crops and Products 74 (2015) 14–19.
- [17] A.M. Barnes, K.D. Bartle, V.R.A. Thibon. A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil, Tribology International 34 (2001) 389–395.
- [18] P.K. Rohatgi, M. Tabandeh-Khorshid, E. Omrani, M.R. Lovell, P.L. Menezes, Tribology for Scientists and Engineers, Springer, New York, 2013 pp. 294-340.
- [19] Y.C. Lin, H. So. Limitations on use of ZDDP as an antiwear additive in boundary lubrication, Tribology International 37 (2004) 25–33.
- [20] U. Choi, B. Ahn, O. Kwon, Y. Chun. Tribological behavior of some antiwear additives in vegetable oils, Tribology International 30 (1997) 677–683.
- [21] T. Chiong Ing, A.K.M. Rafiq, Y. Azli, S. Syahrullail. Tribological behaviour of refined bleached and deodorized palm olein in different loads using a four-ball tribotester, Scientia Iranica 19 (2012) 1487–1492.
- [22] S.Z. Erhan, S. Asadauskas. Lubricant basestocks from vegetable oils, Industrial Crops and Products 11 (2000) 277–282.