International Journal of Engineering Research
Volume No.3, Issue No.8, pp : 494-496
ISSN:2319-6890)(online),2347-5013(print)
01 Aug 2014

Analysis of lubrication properties of zinc-dialkyl-dithio-phosphate (ZDDP) additive on Karanja oil (*Pongamia pinnatta*) as a green lubricant

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Abstract*—*Vegetable oils are biodegradable and renewable compared to mineral based lubricants. But they have some unsatisfactory technological properties. This paper is an attempt to appraise the performance of zinc-dialkyl-dithio-phosphate (ZDDP) as additive in Karanja oil to improve its anti-wear and anti-friction properties. The experiments revealed that the additive (ZDDP) added Karanja oil shows better anti-wear and anti-friction properties. Comparative analyses were conducted on the tribological, physical and chemical properties of Karanja oil and additive-added oil (Karanja oil + 2.0 Wt. % ZDDP) and the mineral oil graded SAE20W40. The tribological properties of these oils were evaluated as per ASTM D4172 B. The tribological results of Karanja oil with 2.0 Wt. % ZDDP shows lower values of Coefficient of friction and Wear scar diameter as compared to generally used mineral based oil SAE20W40. The chemical and physical properties of the this oil was also evaluated by following international standard procedure and showed better results as compared to generally used mineral based oil SAE20W40.

Keywords—Vegetable oil, wear scar diameter, anti-friction, anti-wear, viscosity index, four ball tester, coefficient of friction, lubricating oil.

I. Introduction

Environmental pollution is a major concern when petroleum based lubricants are used in industries [1]. The effluents produced and their subsequent disposal cause severe environmental hazards especially in the hydraulic, mining, agriculture and petrochemical industries. The mineral based oils cannot be used in food industry because of their toxic nature [2]. Vegetable oils with high oleic acid content are the preferred substitute for mineral oils in industries. Vegetable oils are preferred to synthetic fluids because they are renewable, economic and eco-friendly [3]. Furthermore, vegetable oil lubricants are biodegradable and non-toxic unlike conventional mineral based oils. They have low volatility due to high molecular weight of the triacylglycerol molecule and have a narrow range of viscosity changes with temperature i.e. they have high value of viscosity index [4]. Polar ester groups are able to adhere to metal surfaces and therefore, possess good boundary lubrication properties with low coefficient of friction. ZDDP has high dispersion ability in vegetable oils due to high fluidity and surface energy [5]. This paper deals with the improvement of the anti-wear and anti-friction properties of Karanja oil by adding ZDDP for the development of alternative lubricant with good tribological characteristics [6]. New methods to improve the stability of vegetable oils are available, such as the use of additives or modifications to the fatty acid composition (estolides) [7]. Current state of knowledge of each of the main facts of ZDDP behaviour both in solution and at metal surfaces is identified and discussed [8]. Analysis on films from worn samples and engine components confirmed the presence of similar organo-metallic compounds. When combined with reaction films form anti-wear additive such as ZDDP, the soft organo-metallic compounds provide an easily shearable sacrificial layer and the inorganic phosphate glassy structure provides the load carrying capacity. The resultant boundary film is stronger and durable. This understanding provides a design guideline for future boundary films [9]. Wear tests were performed to map effects of load and sliding speed on formation and tribological properties of ZDDP additive anti-wear tribo films formed on steel ball in 2.0 wt% ZDDP added sample of lubricant oil using a high precision four ball tester. Wear film formation was characterized by monitoring the evaluation of coefficient of friction (μ) and wear scar diameter (WSD) [10].

II. Material and Methodology

The equipment used for the experiments include: 1) Four Ball tester TR-30L-PNU-IAS DUCOM and 2) BROOKFIELD DV2T Extra viscometer. Coefficient of friction (COF), wear scar diameter (WSD) and viscosity tests were conducted for Karanja oil, mineral oil and additive added Karanja oil (karanja oil + ZDDP with weight percentage 1.0, 1.5, 2.0, 2.5, 3.0). Anti friction and anti wear properties were analyzed using four ball testers with test conditions 392N load, 75^0C, 1200 RPM and 3600 seconds [10]. For this testing purpose, chromium alloy steel ball as per ASTM D 2783 (IP 239) were used (ANSI standard steel no. E5100), with diameter of 12.7 mm, 64 HN (Hardness Number) and extra polished. Three balls were fixed in a ball pot and one ball at the motor spindle. Viscosity index was calculated by international standard procedure ASTM D 2270-04 [11]. For this calculation the kinematic viscosity of oils at 40^0C and 100^0C were determined using viscometer with international standard viscometer [12]. Chemical properties of oils were analyzed as per American oil chemists' society (AOCS) method [13-16]. Physical properties of oils were determined as per international standard procedure ASTM [17-19].

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III. Results and Tables

1. Effect of ZDDP on anti-wear properties

Wear scar diameter of Karanja oil was found to be decreasing with increasing concentration of the ZDDP additive up to a particular limit. Karanja oil + 2.0 Wt. % ZDDP shows lower value of wear scar diameter. This is due to the anti-wear property of ZDDP, which is effected by (i) mechanically protective film formation (ii) removing corrosive peroxides (iii) by digesting hard and abrasive iron oxides. Most generally the ZDDP forms a reaction film which act as mechanically protective barrier preventing the direct contact between the metal surfaces. The protective layer will act as a cushion between the metal surfaces, so this will help to reduce the stresses between the contacting surfaces. Hence it will help to reduce the wear scar diameter of the steel balls [20]. The second anti-wear mechanism of ZDDP is the reaction with peroxides present in lubricants to prevent the formation of corrosive wearing at the metal surfaces [21-22]. The third anti- wear mechanism is to react with iron oxides present in the base oils to form an iron phosphate which can help to reduce the wear on the metal surfaces [23-25]. At higher concentration the hydrodynamic film formation is hampered, and the zinc contained in ZDDP due to its high density and heavier structure will adhere to metal surface, leading to increase in the wear scar diameter of the contacting surfaces. The wear scar diameter of karanja oil, additive added fluids and mineral oil is shown in Figure 1 and Table 1.

2. Effect of ZDDP in anti-friction properties

The anti friction property of the Karanja oil is found to increase with increasing concentration of ZDDP. This is due to ZDDP forming a hydrodynamic boundary film at a particular concentration (2.0%). At this concentration frictional torque on the contacting surfaces will be reduced and the coefficient of friction at the contact surfaces will also be reduced. But at higher concentration the excess ZDDP adversely affect on the boundary film formation, due to the excess zinc adsorption on the contact surfaces leading to an increase in the frictional torque at higher concentration. The value of coefficient of friction of additive added fluids and Karanja oil is shown in Figure 2 and Table 1.

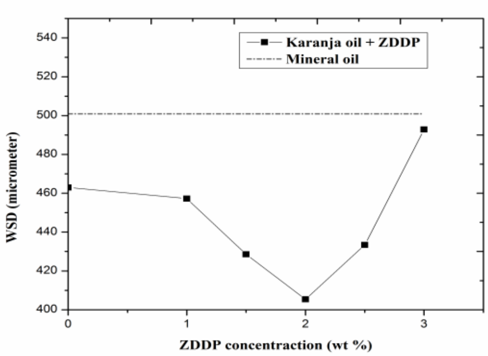

Figure 1: The relation between additive (ZDDP) concentration and wear scar diameter at standard condition.

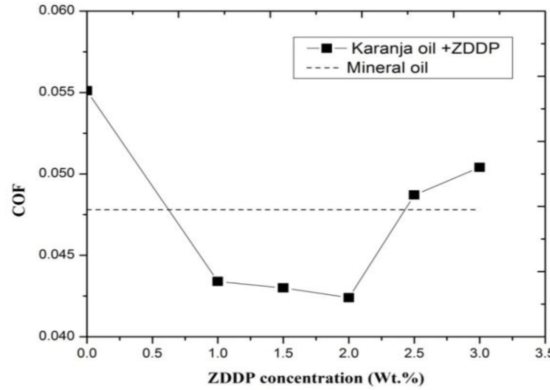

Figure 2: The relation between additive (ZDDP) concentration and coefficient of friction at standard condition.

Oil name	Coefficient of friction (COF)	Wear scar diameter (WSD) in micrometer	Viscosity index
Karanja oil	0.0551	462.99	146
Servo oil	0.0478	500.89	123
Karanja oil + 1.0% ZDDP	0.0434	457.23	162
Karanja oil + 1.5% ZDDP	0.0430	428.56	152
Karanja oil + 2.0% ZDDP	0.0424	405.35	155
Karanja oil + 2.5% ZDDP	0.0487	433.43	157
Karanja oil + 3.0% ZDDP	0.0504	492.87	153

Table 1: Coefficient of friction, wear scar diameter and viscosity index values of karanja oil, karanja oil + ZDDP additive and servo oil

3. Effect of ZDDP on chemical properties

The chemical properties of Karanja oil are affected by adding ZDDP additive. This additive will enhance the saponification value and reduce the acid and iodine values. The saponification value, iodine value, acid value and ester values of Karanja oil and Karanja oil + 2.0% ZDDP liquid additive as shown in Table 2.

Oil name	Saponification value	Iodine value	Acid value	Ester value
Karanja oil	195	86.5	5.6	189.4
Karanja oil + 2.0 % CuO	209	75.3	4.9	204.1

Table 2: Chemical properties of Karanja oil and Karanja oil + 2.0 Wt. % ZDDP

4. Effect of ZDDP on thermal properties

The thermal properties of vegetable oil are affected by adding ZDDP additive. The ZDDP additive has better thermal properties, so it will increase the thermal properties of the oil. The thermal properties of Karanja oil, Karanja oil + 2.0 % ZDDP and mineral oil shown in Table 3.

Oil name	flash point in °C	fire point in °C	pour point in °C	Cloud point in °C
Mineral oil	230	260	-6	-3
Karanja oil	251	260	1	4
Karanja oil + 2.0 % ZDDP	254	266	1	3

Table 3: Thermal properties of mineral, Karanja oil and Karanja oil + 2.0 % ZDDP

III. Conclusion

The tribological tests showed that Karanja oil with 2% ZDDP had comparatively better coefficient friction (μ=0.0424) and wear scar diameter (WSD=405.35 micrometer) than the commercial SAE 20W40 oil tested for comparison (μ=0.0478, WSD=500.89 micrometer). Karanja oil with 2% ZDDP showed a viscosity index of (155) which is higher than that of SAE grade 20W40 oil (123). Flash point and fire point of additive added Karanja oil have higher values (254 & 266) compared to SAE 20W40 (230 &260). Pour point and cloud point were found to be higher than that of the mineral oil. This is the major disadvantage of vegetable oil based lubricants. The four ball and viscometer tests are easy and accurate to evaluate the tribological properties of oil. This will help the industry to introduce new green lubricants by evaluating different oil properties for different applications.

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