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A REVIEW ON ADDITION OF ZINC DIALKYLDITHIOPHOSPHATE IN VEGETABLE OIL AS PHYSICAL PROPERTIES IMPROVER

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ABSTRACT

The need of searching for an alternative for lubricant oil has been studied by a number of researchers due to the awareness of environmental issues. However, with the limitations of low oxidation stability, many straight vegetable oil needs to be added with certain additive in order to improve the performance as lubricant oil. This paper reviews the addition of Zinc Dialkyldithiophosphate (ZDDP) in straight vegetable oil namely canola oil, corn oil and karanja oil. The property improvement upon addition of ZDDP was also reported in this review paper. With the addition of ZDDP in straight vegetable oil is hoped to contribute to the development of a more stable bio-lubricant that could be used in lubricating machines.

Keyword: Zinc Dialkyldithiophosphate (ZDDP), canola oil, corn oil, karanja oil, bio-lubricant.

1. INTRODUCTION

Vegetable oil has been used as lubricant for a long time. According to Gawrillaw (2003), olive oil was used as lubricant to lubricate machineries since 1650BC. However, there is a limitation of using vegetable oil as lubricant because the characteristic of vegetable oil is low oxidation. This statement was supported by Cheenkachorna (2013), where he stated that an inherent property of vegetable oils is low oxidative stability. The low oxidation stability of vegetable oils is due to their unsaturated double bonds exist in the fatty acids and it is said to be an active sites for many reactions, including oxidation. The higher the number of double bonds exist, the greater the level of unsaturation that is, the more susceptible the oil to become oxidation (Azhari *et al.* 2014.

Therefore, adding additive in the vegetable oil is one of the solutions. The additive that suitable to overcome the oxidation is Zinc Dialkyldithiophospate (ZDDP). A research by Johnson *et al.* 1986 found that the interactions between ZDDP and oxidation products were thought to have led to the observed decrease in activity. This statement also been supported by Barnes *et al.* 2001, it stated that ZDDPs were used mainly for their antioxidant properties and their ability to prevent wear.

According to Chang *et al.* 2013 Zinc dialkly dithiophosphate (ZDDP) consists of zinc bound to diphosphordithioic acid with alkyl or alkaryl ester substituent groups. The alkyl groups are saturated hydrocarbons that vary in length from C3- C12. The basic chemical structure of ZDDP is shown in Figure-1.

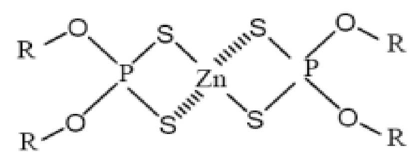

Figure-1. Chemical structure of ZDDP (Chang, 2011).

There are two different ways how antioxidants act, first by radical scavenging. Radical scavengers react with peroxy radicals thus preventing further propagation of the free radical chain. Second is by inhibition of peroxides. Peroxide inhibitors react with hydroperoxide molecules prevent formation of the peroxy radicals Barnes, *et al*. 2001.

The ZDDP complexes are synthesized by reacting phosphorous pentasulfide (P_2S_5) with one or more primary or secondary C3-C10 branched or linear alcohols to form the phosphorodithioic acid ester. The only exception is the alkaryl dithiophosphate where the alcohol moiety is tetrapropenylphenol. The dithiophosphoric acid ester is further diluted with 10-15 wt-% highly refined lubricating base oil, before it is neutralized with zinc oxide. The oil acts as a solvent in the neutralization reaction, manages the viscosity of the final product and improves consistency. The zinc complex that is formed upon neutralization is not a salt in the traditional sense, since the Zn-S bond is more coordinate covalent in character than ionic. (Mahdi *et al.* 2012), the synthesis of ZDDP is shown in Figure-2.

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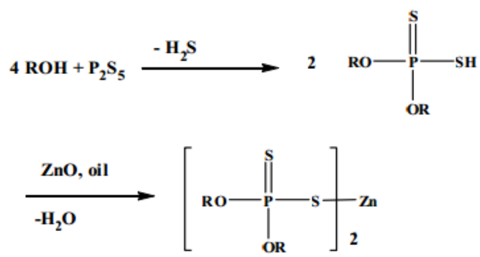

Figure-2. Synthesize of ZDDP (Barnes *et al.* 2001).

According to Ekot *et al.* 2014, ZDDP appears as gold colored liquids with a thickness or viscosity similar to heavy syrup, it is also oil soluble compounds. In one study by Mahdi,. *et al.* 2012 also stated that ZDDP is readily soluble in oil but not soluble in water because ZDDP is denser than water, it will sink in a water environment. The physicochemical properties of zinc dialkyldithiophosphates largely reflect those of base oil. These materials have limited water solubility, low vapor pressure, high viscosity and partition preferentially into the hydrophobic (oil) phase.

However, there is still limitation of using ZDDP. The limitation is based on the concentration. If there is too much concentration, it will cause different wear behavior. By adding ZDDP, it will enhance the formation of film to prevent wear Burkinshaw (2014). However, when the concentration is too high it will increase the thickness of film and decrease the performance as anti-wear.

Therefore, in this study, it will show the effectiveness of ZDDP when blending to vegetable oil and act as lubricant.

2. ZDDP IN VEGETABLE OIL

a) Canola oil

Zainal. 2015, investigated the physical property of canola oil when blended with ZDDP as additive. From this particular study, the sample had been prepared with 0 wt%, 2 wt% and 5 wt% concentration by using direct injection method. In order to determine the concentration of percentage zinc and phosphorus, rotating disc electrode was used and the sample had been used to determine the kinematic viscosity using heated viscometer.

The result reported that the concentration of phosphorus and zinc increased when the concentration of ZDDP which had been blended was increased. The increment of Zinc and Phosphorus was basically from ZDDP where it consisted of phosphorus pentasulfide and addition of zinc. The concentration of zinc was lower than 1ppm at 0wt% concentration of ZDDP and for phosphorous was 14 ppm,by increasing the concentration ZDDP to 2 wt% the concentration of zinc also increased to 1412 ppm from lower than 1 ppm. The concentration of phosphorous also increased as the concentration of ZDDP was increased from 14 ppm to 1399 ppm. For the 5 wt% concentration of ZDDP, the value for zinc and phosphorus kept on increasing. For zinc, the concentration increased from 1412 ppm to 2816 ppm and for phosphorus the concentration increased from 1399 ppm to 3894 ppm.

Based on the result obtained the kinematic viscosity of the prepared sample decreased from 0 wt% concentration of ZDDP to 2 wt% concentration of ZDDP. The value decreased from 40.33 cSt to 38.63 cSt. Then, at 5 wt% concentration the graph showed the value of kinematic viscosity rose drastically from 38.63 cSt to 43.73 cSt

b) Karanja oil

In the study by Mahipal *et al.* 2014, they analyzed the lubricant properties of zinc dialkyldithiophosphate (ZDDP) additive on Karanja oil. In this study, they use experimental method to determine the Coefficient of friction (COF), wear scar diameter (WSD) and viscosity.

In this study the prepared 7 sample which is karanja oil, mineral oil and karanja oil with 5 different weight percentage of ZDDP, which is 1.0 wt% , 1.5 wt%, 2.0 wt%, 2.5 wt% and 3.0 wt%

The results by Mahipal *et al.* (2014) showed that, for mineral oil the wear scar diameter is 500.89µm and the wear scar diameter obtain for karanja oil without additive is 462.99µm. However by adding ZDDP in the karanja oil, the result showed the decreasing value for the wear scar diameter with the increment of concentration of ZDDP. The values of wear scar diameters are decreasing from 457.23µm at 1.0 wt% concentration of ZDDP, 428.56 µm at 1. 5 wt% concentration of ZDDP, and 405.35 µm at 2.0 wt% concentration of ZDDP. The lowest value for wear scar diameter was observed when the oil was added with 2.0 wt% ZDDP. Then, the wear scar diameter staredt to increase back, as the concentration of ZDDP exceeds 2 wt%. The wear Scar diameter are increasing from 405.35µm to 433.43µm as the concentration of ZDDP increasing to 2.5 and for the 3.0 concentration of ZDDP, the value for wear scar diameter are drastically increase to 492.87µm .

The coefficient of friction also correlates with the result of wear scar diameter, where the value of coefficient friction reduced until the concentration of ZDDP reaches 2.0wt%. The values for coefficient friction are sharply drop from 0.0551 at zero concentration to 0.0434 at 1wt% concentration of ZDDP. Then at 1.5wt% concentration of ZDDP the value of coefficient friction is steadily drop to 0.0430, and at 2.0wt% concentration ZDDP, the coefficient friction are slightly decrease until 0.0424. After which, at 2.5wt% concentration of ZDDP the value of coefficient friction start to increase until 0.0487, then the value of coefficient friction steadily increased to 0.0504 at 3.0 wt% concentration of ZDDP. For the mineral oil the value for coefficient friction is 0.0478.

c) Corn oil

Suffian (2015) in her studies prepared 3 samples with different concentration of ZDDP added into corn oil. The 3 concentration are 0 wt%, 2 wt% and 5 wt% of ZDDP. The samples were tested for kinematic viscosity

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and characterized using a pin on disc tribometer at 4 different loads.

From this study, the result showed fluctuation value of viscosity as the concentration increase. The viscosity decreased from 37.3 cSt at zero concentration of ZDDP to 36.3 cSt at 2 wt% concentration. However it increased back as the concentration increased at 5wt% concentration. It increased from 36.3cSt to 37.9 cSt.

This study also showed the result of the effect on ZDDP concentration to coefficient friction, the lowest value of coefficient friction was at 2 wt% concentration of ZDDP. The value of coefficient friction was 0.42 when 5N of load was applied, then the values continued to decrease as the load increased. At 10N load, the coefficient friction was 0.36, then, continued to decrease to 0.34 at 15N and lastly the coefficient friction was just the same value of 0.34 at 20N.

For 5 wt% concentration, the value of coefficients friction also decreased. However the values started to decrease from 0.51 at 5N load, then the value continued to decrease to 0.50 as the load was increased to 10 N. Then, at 15N the value of coefficient friction still decreased to 0.47 and for 20N the coefficient friction increased to 0.48.

For 0 wt% concentration of ZDDP, it showed the highest coefficient friction value where at 5N, the value of coefficient friction was 0.57, then at 10N the value continued to increase up to 0.60, and at 20N the value of coefficient friction continued to also increase up to 0.62. Lastly at 20N the coefficient friction dropped to 0.61.

It was concluded by Suffian (2014) that the desired concentration of ZDDP to be added to corn oil is at 2 wt%. This is evident through the low kinematic viscosity and coefficient of friction displayed by corn oil with the addition of 2 wt% concentration of ZDDP.

d) Mechanism of ZDDP

The fundamental mechanism of ZDDP as anti-wear is the reaction of ZDDP with the metal surface to form a solid protective film and the reaction layer. When metal is immersed in ZDDP solution in a lubricant or other non-polar solvent, a thermal film rapidly forms at the metal surface. Apparently, these films are not simply zinc phosphate, zinc phosphide or iron phosphate (Bird, 1976). Figure-3 below showed the layered structure of surface film formed from ZDDP.

The protective film and the reaction layer formation by ZDDP have four-step processes as shown below.

- Break in
- Physical or chemical adsorption
- Additive-surface reaction
- Reaction layer growth

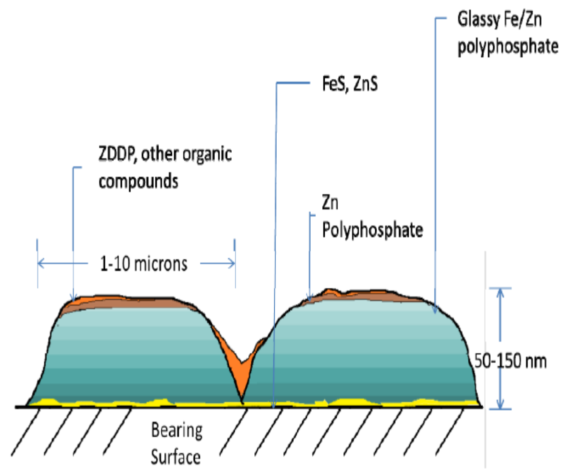

Figure-3. Layered structure of surface film formed from ZDDP (David & Hills, 2013).

Absorption of ZDDP to iron surface occurs first and is followed by the chemical reaction to form a zinc metaphosphate film. Under extreme pressure, an EP film containing sulfur and phosphorous forms (Zen-Yu Chang,2011). The reactions are as depicted in Figure 4 below.

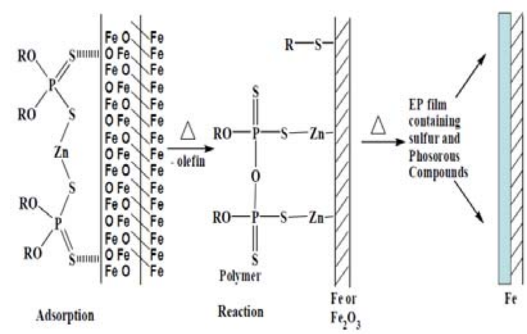

Figure-4. Antiwear mechanisms of boundary film formation by dithiophosphate derviatives (Chang, 1986).

This mechanism explains the process when ZDDP is added. It shows a better result for anti-wear properties and coefficient of friction. Similar results were displayed for all research that had been discussed, by adding ZDDP to base oil. It is observed that the value for anti-wear properties and the coefficient friction will be improved compared with base vegetable oil without any addition of ZDDP as additive. However, if the concentration of ZDDP is too high, it will lead to increment of the wear scar diameter and the coefficient friction. This is because at higher concentration, boundary film formation is affected by excess ZDDP. More film is formed on metal, with the increment of weight percentage of the oil (Azhari *et al.* 2014). Study by Mahipal *et al.*(2014) also stated the increment in the wear scar diameter at connecting surface is due to the hydrodynamic film formation when it is hampered at higher concentration and also the zinc in ZDDP due to its high density and heavier structure.

This is because the formation of film by ZDDP will act as friction reducer, however only the right amount will give better result of kinematic viscosity which is 2 wt% concentration of ZDDP (Mahiapal *et al.*2014)

On the other hand, if the concentration is too high, ZDDP will create more film on metal surface. The increment of viscosity may be contributed due to excess of the metal present (Hutchings, 1992).

There are slightly differences between oils used with ZDDP and without ZDDP on coefficient of friction because of the boundary layer formed by vegetable oils. Clancy (2013) suggested that vegetables alone are more efficient in decreasing friction than the films created by vegetable oils with the ZDDP additive.

By using XANES spectroscopy it can be summarized that ZDDP created tribofilm to oils which is presence of phosphorus species although ZDDP did not greatly affected the lubricity. However, in efficiency of lubricant test, oils without ZDDP showed more potential Result obtained from measure wear scar width both mineral oil with ZDDP or without ZDDP concluded wear scar for mineral without ZDDP higher than mineral oil with ZDDP (Clancy, 2013)

3. CONCLUSIONS

In conclusion, addition of ZDDP as additive in lubricant will give better performance and act as an improver of physical properties in certain vegetables oil and other additives compare to vegetables oils without ZDDP. Based on result that been discussed above viscosity, coefficient of friction, and wear scar diameter of Canola oil, Karanja oil and Corn oil, shows the same result which is its work at better performance at 2.0 wt% concentration of ZDDP.

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