BIO-LUBRICANTS DEVELOPMENT:
REDUCING WEAR SCAR DIAMETERS USING ASHLESS ADDITIVES

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Abstract

An environmentally friendly lube oil was prepared from glycerol and oleic acid. The lube oil viscosity has met the specifications of SAE 50/SAE 90W/ISO VG-150; however, the wear preventive characteristic needed to be improved. Lube oil formulations using various ashless antiwear agents were carried out. The additives used were benzotriazol, elemental sulphur, dibutyl phosphite, 2,5-dimercapto-1,3,4-thiadiazol and combinations thereof. The performance of the formulas was represented by wear scar diameters (WSDs), which were measured by the four ball wear tester (ASTM D-4172). Experimental results showed that all formulations successfully improved the wear properties. The WSDs were reduced from 0.84 mm to 0.34 – 0.75 mm, which were comparable to those of commercial lube oils. The results also indicated that a) dibutyl phosphite was so far the best additive, b) no sinergystic effects were shown from the use of additive mixtures, c) formulation with dibutyl phosphite - benzotriazol mixture resulted in lube oil with a low WSD and less corrosiveness.

Keywords*: bio-lubricants, ashless antiwear agent, wear scar diameter*

1 INTRODUCTION

Lubricants are substances used to separate two surfaces in relative movement one another. Their main function is to avoid direct contact between these surfaces to prevent wear and friction. Lubricants can also function as coolant, sealant, prevent corrosion, and to reduce noise. They can be solid, liquid, or gas. This paper discusses liquid lubricants or lubricating oil which accounts for approximately 90% of total lubricant consumption.

In general, desired properties of lubricating oil can be classified as:

a. Bulk properties, which mainly related to viscosity. Lubricating oil for specific application shall meet proper *viscosity grade* recommended by the *original engine manufacturer* (OEM). In automotive application which operates at wide range of temperature, it is important that the oil have high *viscosity index*, i.e. high stability to temperature change. Viscosity loss due to shear stress (*shear thinning*) is undesired.
b. Chemical properties related to oxidation stability. Lube oil with higher stability have better chance for longer service life. Oxidation may convert lube oil to higher viscosity product, sludge and deposit formation. Oxidation can also increase corrosiveness which harmful to machine element due to organic acid formation.
c. Surface chemistry properties. Lube oil shall gave low friction coefficient and protect surface against wear.
d. Other properties which can be regarded as minor problem and/or application-specific such as low foaming tendency, low volatility, good detergency and dispersancy, demulsification, and seal compatibility.

The increase in environmental and energy awareness nowadays demands the use of substitute materials and the utilization of more energy conserving and sound environmental processes. Lube oil derived from vegetable oil may serve as alternative source for lube oil base stock which conventionally derived from mineral oil. These *bio-based* product is renewable and intrinsically free from *sulfated ash*/*phosphorus*/*sulfur* (SAPS) which considered harmful to the environment and lubricant formulation trend is to reduce them. (Carnes, 2005; Canter, 2006).

We have been working to build reaction path process synthesis and product development to create lubricating oil base stock based on oleo-chemical chemistry. While the design of viscosity and improvement of oxidation stability was reported earlier (Dermawan et.al 2004, 2010), this paper reports an experimental study in improving its ability to protect contacting surfaces against wear.

Wear is loss of material from the surface caused by mechanical process, i.e. contact and relative movement between two surfaces. Even the smoothest surfaces as we perceive will look so rough in microscopic scale that is consist of valleys and hills called *asperity*. In hydrodynamic lubrication (Fig. 1) where the interacting surfaces completely separated by thick oil film, no direct contact take place and wear does not occur. Increase in load reduce the oil film thickness and shift the lubrication regime to *mixed lubrication* allowing *contact asperity* results in wear, increased friction coefficient and heat generation. In *boundary lubrication* where oil viscosity is no longer governing, heat generated by friction may be high enough to cause local welding: relative movement between contacting surfaces will be very resisted, friction coefficient increase tremendously causing failure of machine element to function properly.

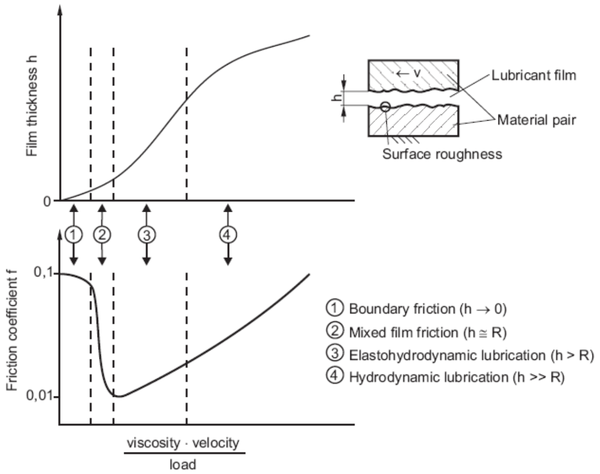

Figure 1 Lubrication Regimes: Stribeck Curve (Mang, 2007)

Lubricating oil control wear by forming adsorbed film so that direct contact between metal surfaces can be avoided. The ability of film formation originated from a class of components in lubricating oil formulation called antiwear agent, abbrev. AW. These additives not only absorb onto the metal surface, but also react further in the case of a thermal fragmentation or tribofragmentation reaction, building a chemical reaction layer on the metal. The formed layers make the tribological contact softer, preventing a direct metal-to-metal contact of moving metal parts. AW additives are used for applications with medium loads. One model to explain the mode of action of these additives is to assume that polymer condensation and polymerization reactions are initiated, which provide a protecting layer on the metal. This layer is sheared off and renewed constantly during the operation. Under very high loads, the performance of AW additives becomes insufficient and designated EP additives are needed. These additives undergo real reactions with the metal surface to form tribolayers consisting of iron phosphite or iron sulfides or iron chlorides. Here, the metal is a part of the protective tribolayer. (Habereder et.al, 2009). The distinction between AW and EP is not clear-cut.

Performance of an AW additive is strongly depends on interaction between the additive, base oil, other components in the formulation, and applied metallic surface. In polar esters, lube oil interact strongly with metal surfaces and consequently provide an already good protection against friction and wear, at least under mild conditions. For more demanding applications, in which the protective reaction layer provided from additives is required, the high surface activity of the base oil is detrimental, as the additives are hindered to approach the metal surface in the first stage. Hence, higher treat rates of additives need to be applied, and preferentially more polar additives have to be used (Habereder, 2009).

Zinc dialkyldithiophosphates (ZnDTPs) has long been used as single most important antiwear agent for over 60 years now. They are used in practically all lubricating oil performance package for their performance and cost effectiveness. In addition to antiwear, ZnDTPs also perform as antioxidant and metal passivator. However, Minami & Mitsumune (2002) showed that performance of ZnDTPs are less effective in polar base oils such as esters and their action are inhibited by degradation product of vegetable oil. Furthermore, their incompatibility with catalytic converter prompts the exploration for alternative antiwear agents.

Antiwear agents generally classified as metal-containing or ashless. Ashless additives are further divided by elements: sulfur, phosphorus, nitrogen, halogen, and combinations thereof. Ashless additives are preferred because of their low toxicity level and they do not contribute to sulfated ash content. In this experiment we use several tipes of ashless antiwear agent: 1) dibutyl phosphite, a phosphorus-containing additive, 2) elemental sulfur, 3) benzotriazol, a nitrogen-containing additive, and 4) 2,5-dimercapto-1,3,4-thiadiazol (DMTD), an additive containing both nitrogen and sulfur, to improve antiwear properties of our experimental bio-based lubricating oil that meet SAE 50/SAE 90W/ISO VG-150 viscosity grade specifications.

2 METHODOLOGY

2.1 Material

Glycerine, oleic acid, caustic soda catalyst, natural zeolite, and elemental sulfur used are technical grades bought from Brataco Chemika, Bandung, a local chemical grocery store. Phenyl-α-naphtylamine 98% (CAS 90-30-2), 4,4'-methylenebis(2,6-di-tert-butyl-phenol) 98% (CAS 118-82-1), silicon oil DC 200 (CAS 63148-62-9), dibutyl phosphite 96% (CAS 1089-19-4), benzotriazol 99% (CAS 95-14-7) and 2,5-dimercapto-1,3,4-thiadiazol 98% (CAS 1072-71-5) are from Aldrich. All are used without any treatment.

2.2 Bio-lubricant

The bio-based lubricating oil used is a complex esters derived from glycerol and oleic acid. The process for preparation of this oil essentially consists of 3 reaction steps: (1) glycerol dehydration,

(2) stabilization of oleic acid, and (3) esterification of reaction products of (1) and (2).

Glycerol dehydration is carried out in inert nitrogen atmosphere at 250^o for 2-3 hours using 1 wt% caustic soda. Stabilization of oleic acid is carried out at 230^{o}C using 5 wt% of natural zeolite for 3 hours. In this step phenyl-α-naphtylamine antioxidant is also introduced at 1,6 wt%. Esterification is carried out in the same manner at reactant weight ratio of 1 : 5 base on initial glycerol/oleic acid reacted. No additional catalyst is used. At the end of esterification process, 0.01 wt% PDMS antifoaming agent and 1 wt% 4,4'-methylene-bis(2,6-di-tert-butyl) phenol antioxidant are also added.

2.3 Formulation

Formulation is carried out by blending the above described oil with selected ashless antiwear agents and combinations thereof. Additive concentrations are determined by maximum allowable level in CJ-4 oil, i.e. 0.12 wt% phosphorus and 0.4% sulfur. Nitrogen level in benzotriazol is arranged so as have the same nitrogen level in formulation with DMTD at 0.4 wt% sulfur. Table 1 summarize variation in additive formulation used throughout this work.

Table 1 Experimental Variation

No.	Antiwear Agent	Element	Concentration
1	No Additive		-
2	Benzotriazol	N	0.331%
3	Sulfur elemental	S	0.400%
4	Dibutyl phosphite	P	0.752%
5	DMTD	N,S	0.626%
6	2 + 3	N - S	
7	2 + 4	N - P	
8	3 + 4	S - P	
9	2 + 3 + 4	N - S - P	
10	4 + 5	N,S - P	

2.4 Wear Test

Wear test is carried out to examine the efficacy of the additives in improving wear protection characteristic. The test is carried out using four ball tester to simulate oil capacity in preventing wear in sliding contact according to Standard Method for Wear Preventive Characteristics of Lubricating Fluid (ASTM D-4172). In summary, three 12.7-mm [1⁄2-in.] diameter steel balls are clamped together and covered with the lubricant to be evaluated. A fourth 12.7–mm diameter steel ball, referred to as the top ball, is pressed with a force 40 kg$_f$ (Option B) into the cavity formed by the three clamped balls for three-point contact. All balls are chromium steel alloy meet AISI No. E-52100 Grade 25 EP (Extra Polish) with Hardness Rockwell C 64 – 66. The temperature of the test lubricant is regulated at (75 ± 2)°C and then the top ball is rotated at (1200 ± 60) rpm for (60 ± 1) min. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls.

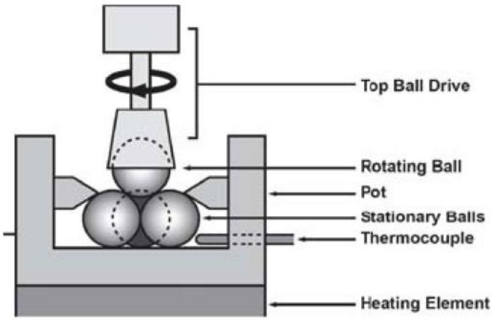

Figure 2 Arrangement of Four Ball Tester

2.5 Corrosion Test

Additive may be reactive enough to corrode metallic surface, lead to dissolution of metallic cations to bulk phase. These cations, in turn, cause detrimental effect by catalyze oxidative degradation of the lubricating oil. To study this possibility, 120 grams of sample is placed in a beaker glass containing cylindrically shaped of copper (166 g, 8 sqin) and steel (245 g, 16 sqin) maintained at 150^{o}C. Air is bubbled in to this glass for 24 hours. Weigh loss of both metal before and after the test are used as estimates for corrosiveness.

3 RESULTS AND DISCUSSIONS

3.1 Effect of Formulation to Kinematic Viscosity

Despite the fact that all additives are used below 1 wt%, some formulation increase kinematic viscosity of the base oil significantly (Table 2). The highest increase is observed in the formulation containing sulfur, indicating that chemical reaction, rather than dissolution of additive, is actually taken place. Viscosity indices generally a bit decrease, except for formulation with elemental sulfur which reaches 7%. Viscosity increase and significant decrease in viscosity index is caused by sulfur action in combining two or more base oil molecules such as that of vulcanization reaction.

Table 2 Effect of Formulation on Kinematic Viscosity

No.	Viscosity @ 40 ^{o}C, cSt	Change	Viscosity @ 100 ^{o}C, cSt	Change	Viscosity Index	Change
1	146	Control	18.6	Control	144	Control
2	153	5%	19.2	4%	143	-1%
3	178	22%	20.4	10%	134	-7%
4	144	-1%	18.6	0%	145	1%
5	173	19%	20.5	11%	138	-4%

6	178	22%	20.9	12%	138	-4%
7	152	4%	19.4	4%	146	2%
8	166	14%	20.1	8%	140	-2%
9	163	12%	20.2	8%	144	0%
10	159	9%	19.7	6%	142	-1%

3.2 Wear Scar Diameter, WSD

WSD is a measure of antiwear property of lubricating oil. Lower WSD means smaller surface scar caused by sliding contact between interacting surfaces at test conditions indicating better antiwear characteristic. After test, all three stationary balls are checked under microscope to measure their scar diameters, both vertically and horizontally. Reported results are averages of all measures. Figure 3 illustrates WSD measurement for the base oil.

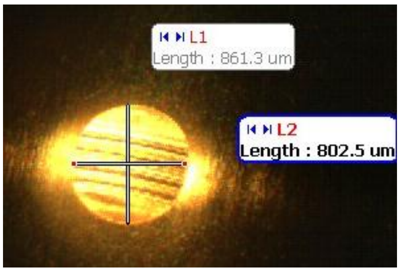

Figure 3 Wear Scar Diameter Measurements for the Base Oil (No Additive)

Figure 4 summarize the effect of formulation to wear preventive property of the base oil. Comparing data no. 1 with data no. 2 – 5 clearly shows that all additive used are successfully improving antiwear property of the oil.

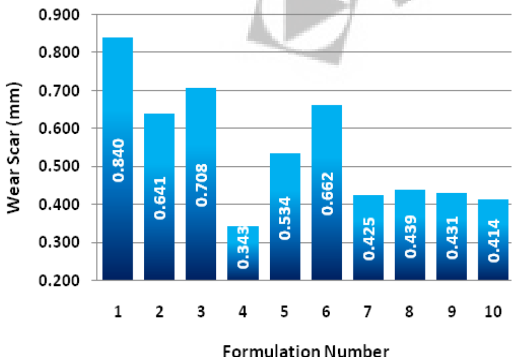

Figure 4 Performance of Ashless Antiwear Agent

It is well known that sulfur containing additives react with ferrous surface to form ferrous sulfide. *Base oil* containing sulfur, due to its polarity, difuse to metalic surface. Heat will decompose the oil, releasing sulfur. Ferrous oxide then replaced by ferrous sulfide. It is surprising that this study show that sulfurized base oil give the least WSD improvement. This might be due to the relatively low temperature of test condition so that only small amount of sulfur decomposed.

DMTD, which contain both N and S atom, in the elemental point of view, can be regarded as a combination of sulfurized base oil which contain S, and benzotriazol, which contain N. DMTD show better performance (WSD = 0.53 mm) than both sulfurized base oil (WSD = 0.75) and benzotriazol (WSD = 0.64 mm). This suggests the existence of synergistic effect between additives. However, this is not observed from data no. 6 – 10 which clearly show the performance of additive combination always positioned between that of the individuals. For example, combination of no. 2 (WSD = 0.64) and no. 3 (WSD = 0.71) results in WSD = 0.66 (no. 6). In other word, additives in mixture do not interact, but tend to compete for surface. Thus, synergistic effect such as those of DMTD can be expected if the components interaction/react to form new, higher surface affinity compound.

Interaction/reaction between additive and base oil may have strong relation with its performance. If the reaction results in lower polarity product, it is likely that its performance will be decrease. As shown in Table 1, dibutyl phosphite is the only additive used that indicate no chemical reaction with the base oil.

Figure 5 show WSDs for several commercial gear oil measured at the same condition published by Amsoil (2007). Thus, formulation in this study, particularly those with dibutyl phosphite and its mixtures gives comparable result with commercial product.

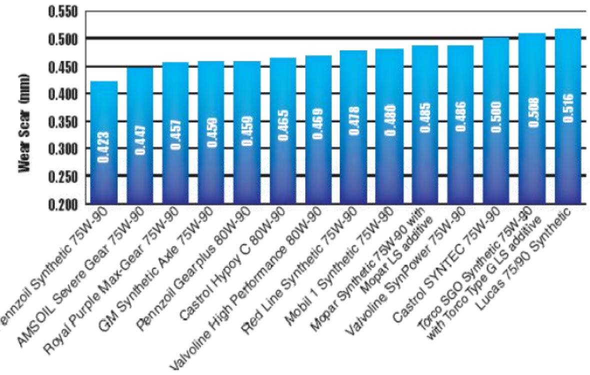

Figure 5 WSDs of Several Commercial Gear Oil

3.3 Rust/Corrosion Prevention

Figure 6 show the effect of formulation to corrosiveness of the lubricating oil. Except for formulation with benzotriazol, all formulation shows weight loss of steel and copper, indicating formulation corrosiveness. Benzotriazol show its property of corrosion inhibitor: adsorbed on metallic surface remain there to prevent the surface from contact with corrosive materials that may corrode the surface, results in weigh increase. On the other hand, other additive seems to react with the surface, eventually oxidize steel and copper surface results in cation dissolution leading to weight loss.

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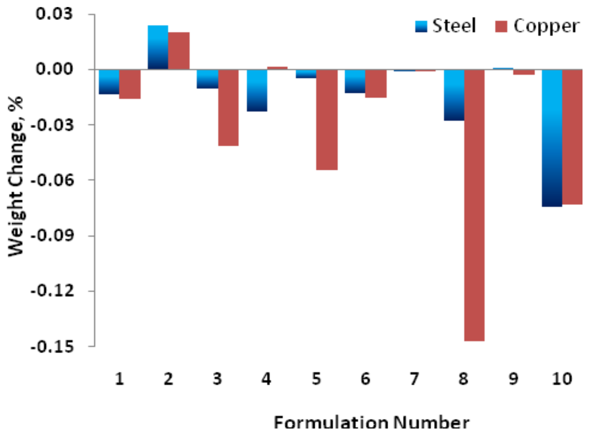

Figure 6 Corrosiveness of Formulation (150^{o}C, 24 h)

Sulfur containing additives (no. 3 and 5) corrosive to copper but does not to steel. On the other hand, dibutyl phosphite corrosive to steel but does not to copper. Combination of these additives (no. 8 and 10) give detrimental effect resuls in even higher corrosivity to both metals. Possibly, at test condition, the additives react to form corrosive phosphorothioate (Farng, 2009). However, this corrosiveness disappears when benzotriazol is added (no. 9) but this is incorporated with decrease in wear property shown as the increase in WSD. Indeed, all combination with benzotriazol (no. 6, 7, and 9) show low corrosiveness, indicating its act as corrosion inhibitor. The presence of N in DMTD does not contribute to corrosion inhibition. In fact, dibutyl phosphite - DMTD mixture (no. 10) results in the most corrosive formulation.

The best additive combination is shown in benzotriazol – dibutyl phosphite mixture (no. 7): dibutyl phosphite responsible for low WSD, while benzoltriazol reduce the corrosiveness of dibutyl phosphite with acceptable impact to WSD. Formulations with elemental sulphur, sole or in combination with other additive, always show detrimental effect on corrosiveness.

4 CONCLUSIONS

An effort has been established to develop environmental friendly lubricating oil derived from glycerol and oleic acid. Blended with phenyl-α-naphtylamine and 4,4’-methylene-bis(2,6-ditert-butyl phenol) antioxidants and small amount of antifoaming agent is the base case of formulation with ashless antiwear agents to improve wear preventive characteristics.

Experimental results showed some promise for further development. All formulations successfully improved the wear properties, showed from WSD decrease from 0.84 mm to 0.34 – 0.75 mm, which were comparable to those of commercial lube oils. The results also indicated that at test condition, a) dibutyl phosphite was so far the best additive, b) no sinergystic effects were shown from the use of AWs mixtures, but single AW with combined elements show different behaviour from mixture of element-containing AWs c) benzotriazol act more as corrosion inhibitor than antiwear agent. Formulation with dibutyl phosphite - benzotriazol mixture resulted in lube oil with a low WSD and with improved rust/corrosion prevention.

5 ACKNOWLEDGEMENT

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