

# Bio-Lubricants Development: The Potential Use of Boron-Containing Additives

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## **Abstract :**

This paper reports the use of boron-containing additives to improve the performance of a bio-based lubricating oil. The base oil was prepared from glycerol and oleic acid, was fortified with antifoaming agent, phenyl- $\alpha$ -naphthylamine, 4,4'-methylene-bis(2,6-ditert-butyl) phenol, and benzotriazol and has met the SAE 90 gear oil viscosity classification. The additives was prepared by reacting boric acid with monoethanolamine and was used in all formulations at 0.01 %wt of boron/kg. The test of extreme pressure property was carried out to examine the load-carrying capacity of the lubricating fluids using the four-ball extreme pressure tester according to ASTM D-2783. The oxidation & corrosion test was carried out using the bulk test at 150°C for 24 h. Steel & copper specimens weight losses were used to estimate the lubricants corrosiveness. Meanwhile, kinematic viscosity increase at 40°C was used to measure the effect of formulation to the oxidation stability of the oil. Experimental results showed that when used alone, the boron-containing additive exhibited antioxidant activity, i.e. prevention of viscosity increases, and protection against corrosions, particularly to copper. The formulation did not show any noticeable effects on extreme pressure characteristics. Nevertheless, when used in combinations with dibutyl phosphite and/or 2,5-dimercapto-1,3,4-thiadiazol, significant improvements in load – wear indices were shown. The best achievement reached a last non-seizure load of 40 kg, a weld point of 400 kg, and a load – wear index of 54.37 – 55.47. The antioxidant activities were decreased when boron was used in combinations with these additives even though their oxidation stabilities were better than that of the base case oil. The combination with 2,5-dimercapto-1,3,4-thiadiazol also showed a better rust/corrosion prevention.

**Keywords:** antioxidant, bio-lubricants, boron, corrosion, extreme pressure.

## **1. Introduction**

Lubricating oil is a functional material applied for separating two surfaces with relative movements one another in order to avoid direct contacts thus reducing frictions and component damages due to wear. According to their sources, lubricating oils can be classified into mineral, synthetic, and bio-based oils. The increasing environmental issues regarding biodegradability, renewability, toxicity and health & safety risks have been gaining attentions towards the development of bio-based lubricants. Some researchers tend to investigate the potential use of sole vegetable oils [1-3] and leave their shortcomings for additive formulations, while others are more interested in chemical modifications of these vegetable oils in order to improve their properties [4-6]. The favorable lube oil properties include both bulk and surface properties; however, it is believed that no single molecule can meet all desired properties. Thus, further formulations using additives are usually required to meet certain application-specific requirements.

We have been working on reaction path process syntheses and on product development to create lubricating oils based on oleo chemical chemistry. Processes for preparing this bio-based lube oil include (1) the dehydration of glycerol, (2) the stability improvement of oleic acid, and (3) the esterification of the aforementioned reactions' products. These processes have succeeded in enabling the preparation of high viscosity index lube oils with wide range of viscosity [7]; however, the need for additives to boost their performances is inevitable. Since an additive performance is a function of the base oil and is affected by other materials in the oil, a formulation study is clearly complex in nature. Multifunctional additives, i.e. additives which give several properties improvements, are preferable. Ashless additives are favored over metal-containing additives for environmental reasons [8].

Our previous study showed that dibutyl phosphite has succeeded in reducing wear scar diameter as measured according to ASTM D-4172. However, in more stringent conditions, known as extreme pressure conditions (as measured according to ASTM D-2783), the dibutyl phosphite needed to be combined with 2,5-dimercapto-1,3,4-thiadiazol (DMTD) to give an acceptable result. Nevertheless, this was followed by an excessive corrosiveness and a decreased oxidation stability [9]. This study is aimed at further formulations for extreme pressure property improvements without any detrimental effects on either the corrosiveness or the oxidation stability. An extreme pressure condition is the most severe case of boundary lubrications. In this condition, heavily

loaded surfaces are exposed to very high local pressures at asperities, which are typically four orders of magnitudes higher than that of the applied load. The heat generated by the local pressure creates a very high local temperature, typically 300 - 1000°C, without a significant increase in the average surrounding temperature [10]. Current extreme pressure additives typically contain chlorine, phosphorus, and/or sulfur. These additives are believed to be activated by high temperatures and react with metallic surfaces, creating a highly resistant tenacious layer which is capable of supporting high loads and thus preventing major wear or breakdown. Their main applications includes gear oils, greases, hydraulic fluids, and metalworking lubricants [11].

Among many interesting alternative additives to examine are boron-containing compounds. Boron esters improve oxidation stability, antiwear, and antifriction properties of lubricants when used alone or in combinations with other additives. Borate esters with nitrogen are known for their antioxidant activities and for improving antiwear properties. The borates do not only inhibit corrosions but also be found to be bacteriostatic (biostatic) agents. A large synergistic inhibitory effect has been found when they are combined with amines [12]. King & Bakker [13] used microparticles of alkaline earth metal borate ( $M_2O \cdot xB_2O_3 \cdot yH_2O$ ), which was made by mixing boric acid with overbased alkaline earth metal sulfonate in a liquid oleophilic media under 0.1 micron. Unlike other extreme pressure additives, these additives were believed be unaffected by temperature and work by depositions at metallic surfaces. Stoffa & Gapinsky [14] claimed that borated overbased sulfonates improves gear performances in functional fluids. According to Tipton [15], overbased carboxylates, especially those borated, are effective corrosion inhibitors for gear oils. Also, there were no antagonistic effects on their protective actions towards shock loadings and no detrimental effects on thermal/oxidation stability as generally shown by aminic compounds. Zehler [16] formulated extreme pressure lubricants containing 1 – 3 %wt EP Lubrizol 5045 containing 0.36 %wt boron, 1.21 %wt nitrogen, 1.61 %wt phosphorus, and 19.6 %wt sulfur. Wang et al. [17] used a novel disulphide compound containing boron showing excellent tribological properties with no noticeable odour, little corrosion to copper, exhibited better thermal stability and antioxidant performance compared to sulfurized olefins. Their study also revealed that tribological reactions occurred between the additive and the metal surface forming a film consisting  $FeSO_4$ . This was also accompanied by the adsorption of decomposed borate ester and organic sulfide. Hu et al. [18] found that boron – nitrogen compounds improve antiwear properties and showed a synergistic effect with ZnDTP and SnDTP in liquid paraffins. Their mechanistic study suggests the formation of protective boron nitride and  $B_2O_3$  at mating surfaces. Shah [19] showed that S-di-n-octoxyboron-O,O'-di-n-octyldithiophosphate gave better wear scar diameters and better friction coefficients in comparison to those of ZDTP. The formulation study of Karol & Donnelly [20] revealed synergistic effects in the combinations of organoborate esters and sulfur- or phosphorus-containing additives such as dithiocarbamate, bisdithiocarbamate, DMTD, phosphorodithioate and their esters, or nonsulfur molybdenum compounds made from a molybdenum source, fatty oil, and diethanolamine.

## 2. Material and Methods

### 2.1. Raw Material

Glycerine, oleic acid, caustic soda, natural zeolite, and elemental sulfur used were of technical grades bought from a local chemical grocery store, Brataco Chemika, Bandung. Phenyl- $\alpha$ -naphthylamine 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), 2,5-dimercapto-1,3,4-thiadiazol 98% (CAS 1072-71-5) and molybdenum (VI) oxide (CAS 1313-27-5) were from Aldrich. Boric acid > 99.5% was from Fluka Chemie AG, and ethanolamine extra pure > 99% was from E.Merck. All were used without any treatments.

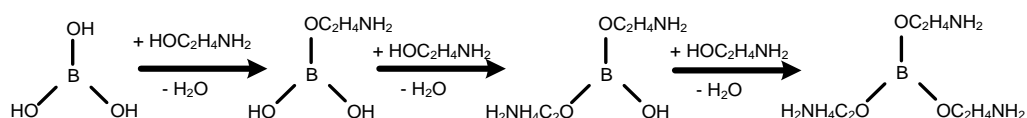
### 2.2. Base Case Oil

The bio-based lubricating oil used was a complex ester derived from glycerol and oleic acid. The process for preparation of this oil essentially consisted of three reaction steps: (1) the glycerol dehydration, (2) the stabilization of oleic acid, and (3) the esterification of reaction products of (1) and (2). The glycerol dehydration was carried out in an inert nitrogen atmosphere at 250°C for 2-3 hours using 1 wt% caustic soda. The stabilization of oleic acid was carried out at 230°C using 5 wt% of natural zeolite for 3 hours. In this step phenyl- $\alpha$ -naphthylamine

antioxidant was also introduced at 1.6 wt%. The esterification was carried out at glycerol/oleic acid weight ratio of 1 : 5. No additional catalyst was used. At the end of the esterification process, 1 wt% of 4,4'-methylene-bis(2,6-di-tert-butyl)phenol antioxidant, 0.01 wt% of silicon oil DC 200, and 0.01% wt of benzotriazol were also added.

### 2.3. Boron Additive

The boron additive should be used in an oil-soluble form. Literature survey reveals that a) boric acid may reacts with alcohol to form boric acid ester b) reactions of boron with nitrogen compounds may results in solid hexagonal boron nitrides, graphite-like soft materials commonly used as solid lubricants [19]. Thus, the boron-containing additive used in this experiment was prepared by reacting a boric acid solution with an excessed monoethanolamine (MEA) according to the following esterification reactions:



Three grams of boric acid, 50 g of MEA and 25 g of water were mixed & heated in an erlenmeyer equipped with a heater and a magnetic stirrer until a clear yellowish solution was formed. The inert nitrogen was sparged to the reactor to avoid contacts with oxygen. Heating and stirring were continued to reach the temperature of 171°C to distill-off all water and parts of MEA. The product was a clear yellowish solution containing 29.5 mg boron per gram (calculated).

### 2.4. Formulation

Formulations were carried out by blending the above described base case oil with the boron-containing additive and by additions of selected ashless antiwear agents. The boron concentration was 0.01 wt%, while the antiwear agents were dibutyl phosphite and/or DMTD. Their concentrations were determined by the maximum allowable level in CJ-4 oils, i.e. 0.12 wt% phosphorus and 0.4 wt% sulfur. Table 1 summarizes the formulations used throughout this work.

**Table 1.** Experimental Variations

No.	Formulation	Concentration
1	No Additive	
2	BMEA	0.345%
3	BMEA + Dibutyl phosphite	0.752%
4	BMEA + DMTD	0.626%
5	BMEA + DMTD + Dibutyl phosphite	

### 2.5. Extreme Pressure Properties Test

The extreme pressure properties test was carried out to examine the load-carrying capacity of the lubricating fluid using four-ball extreme pressure tester according to Standard Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (ASTM D-2783). In this method, three 12.7-mm (1/2-in.) diameter steel balls are clamped together and are covered with the lubricant to be evaluated. The fourth 12.7-mm diameter steel ball, referred to as the top ball, is pressed into the cavity formed by the three clamped balls for a 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 rotating speed is 1760 ± 40 rpm. The temperature of the lubricant is firstly brought to 18 – 35°C and then, a series of tests of 10-s duration is made at increasing loads until welding occurs.

### 2.6. Corrosion and Oxidation Tests

An additive may be reactive enough to corrode metallic surfaces leading to dissolution of metallic cations to the bulk phase. These cations, in turn, cause detrimental effects by catalyzing oxidative degradations of the lubricating oil. In order to examine this possibility, 50 grams of sample is placed in a test tube containing a

cylindrically shaped of copper (166 g, 8 sqin) or steel (245 g, 16 sqin) maintained at 150°C. Air is bubbled into the oil for 24 hours. The weight losses of both metals during the test are used to estimate the lubricant corrosiveness. Kinematic viscosity increases at 40°C are used to measure the effect of formulations to the oxidation stability of the oil.

### 3. Result and Discussion.

Figure 1 depicts the FTIR spectra of the boron-containing additive. Since the additive contained excessive amount of ethanolamine (MEA), this spectra was, as expected, similar to that of MEA (inset). The intensive absorbance was between about 3000  $\text{cm}^{-1}$  - 3600  $\text{cm}^{-1}$ , which was due to N–H and O–H bonds. Another strong absorption region in the range of 1465 – 1330  $\text{cm}^{-1}$  was due to a B–N stretching suggesting strong interaction i.e. a coordinating bond between the electron-deficient boron with non-bonding pairs of nitrogen electrons. A C–N stretching caused a strong absorption peak at 1566.1  $\text{cm}^{-1}$ . The peak characteristic at 1070.4  $\text{cm}^{-1}$  corresponded to a C–N bond (1081  $\text{cm}^{-1}$  for pure MEA). A B–O stretching detected at 1386.7  $\text{cm}^{-1}$ .

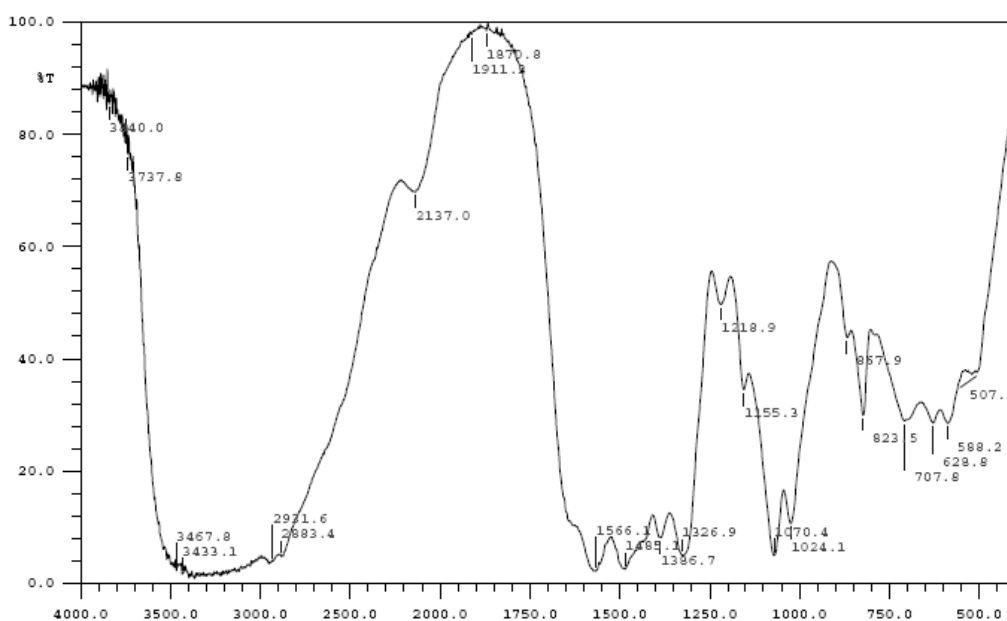


Figure 1. An FTIR Spectra of a BMEA Additive. Inset is That of Pure MEA

#### 3.1. Extreme Pressure Properties

Table 2 summarizes the results of four-ball extreme pressure tests. Data comparison for formulations no. 1 and no. 2 reveals that the additions of boron did not contribute to any improvements, either to the last-non seizure load or to the weld point. Moreover, there was only a small decrease in the load – wear index. Thus, the formation of hexagonal boron nitride or  $\text{B}_2\text{O}_3$  from the corresponding decomposed additives might not take place. However, as shown in Fig. 2, as we used the additive in combinations with dibutyl phosphite and/or DMTD, either dibutyl phosphite or DMTD and their combinations showed better performances in comparison to their corresponding performances when no BMEA present as previously reported [9]. This suggests that some kind of interaction arrangement was taking place. One possible explanation is that boron was acting as a coordinating atom. Mosey et al. [21] used the argument of pressure-activated change in coordination number to explain the role of zinc in relation to the findings that the performance of zinc dithiophosphate was always superior to their corresponding ashless dithiophosphate.

**Table 2.** Summary of Four-Ball EP Test Results of Lubricants with Boron-containing Additives

Formulation No.	Last Non-Seizure Load, kg	Weld Point, kg	Load-Wear Index
1	40	200	22.85
2	40	200	22.70
3	63	250	32.58
4	80	400	55.47
5	80	400	54.37

As readily seen, the performance improvement by DMTD was greater than that of dibutyl phosphite. In other word, in the absent of BMEA, dibutyl phosphite was a better extreme pressure additive than DMTD but in the presence of BMEA the opposite was true. Moreover, in the present of BMEA, the use of dibutyl phosphite seemed inappropriate as the combination of (dibutyl phosphite + DMTD) addition showed no improvements over those of DMTD addition alone. This gave rise the possibility towards a lower or even zero phosphorus formulation. Phosphorus component is unfavorable due to its poisoning effect to catalyst material in the cars' catalytic converters, which is used to reduce the emission of environmentally damaging gases [22]. However, the need for dibutyl phosphite was suggested by the earlier study, which concludes the necessity of dibutyl phosphite addition to maintain the wear scar diameter low [9]. The needs for dibutyl phosphite addition was also supported by a statement of Karol & Tepper in their patent [23] that even though DMTD addition shows a satisfactory result in the four-ball test, it sometimes gives a poor Timken OK load.

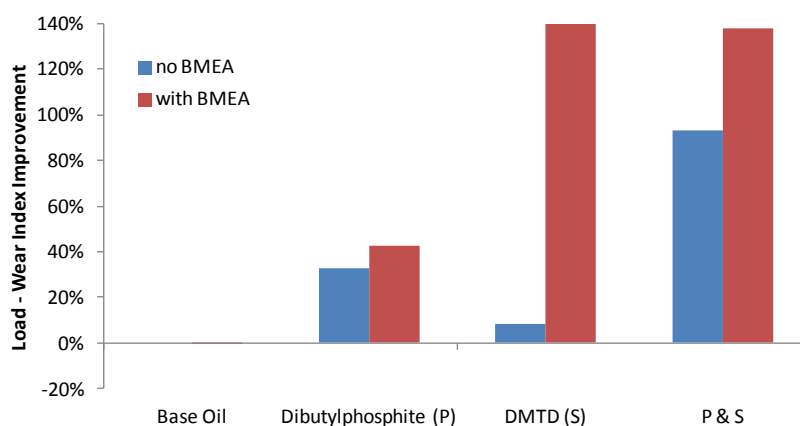


Figure 2. Comparison of Dibutyl Phosphite, DMTD and their Combinations in the Absent (Blue) and in the Present (Red) of BMEA Additives. Load - wear Index Improvement is Calculated Using:

$$\text{LWI Improvement} = \frac{\text{LWI}(\text{formulation}) - \text{LWI}(\text{basecase})}{\text{LWI}(\text{basecase})} \cdot 100\%$$

### 3.2. Corrosiveness and Oxidation Stability

Table 3 summarizes the results of the corrosion/oxidation tests. It shows that the boron-containing additive increases the corrosiveness to steel; however, the lubricant tends to be less corrosive to copper. It also surprisingly shows a high antioxidant activity in term of reductions in kinematic viscosity increase. Data for formulation no. 3 shows that the interaction of BMEA with DMTD resulted in a chemical reaction. It formed solids with rust preventive characteristics which were easily adsorbed on the copper surface resulted in the copper weight increase. The finding that such an interaction did not take place when dibutyl phosphite was further added (formulation no. 5) suggests that in the later case DMTD was first reacted with dibutyl phosphite to form corrosive phosphorothioate [24] which cannot interact with BMEA the way DMTD does. All data shows that the interaction of BMEA with DMTD, dibutyl phosphite, and their combinations resulted in negative impacts on oxidation stabilities. Nevertheless, in all cases, their stabilities were still much better than those of the base case oil.

**Table 3.** Summary of Corrosiveness and Oxidation Stability Test

Formulation No.	Weight Loss of Steel, mg/kg	Weight Loss of Copper, mg/kg	Kinematic Viscosity @40°C Increase, %
1	49	172	616
2	139	86	60
3	131	61	128
4	24	-51	196
5	445	60	225

#### 4. Conclusion

An effort has been made to explore the potential use of boron as an environmental friendly additive for a bio-based lubricating oil. The base case oil was derived from glycerol and oleic acid, and was fortified with antifoaming agent, phenyl- $\alpha$ -naphthylamine, 4,4'-methylene-bis(2,6-ditert-butyl) phenol, and benzotriazol. In addition, it has met the SAE 90 gear oil viscosity classification. Experimental results showed that the use of 0.01 wt% boron, in the form of an additive prepared by reacting boric acid with monoethanolamine, exhibited antioxidant activity in terms of viscosity increased prevention and protection against corrosion, particularly to copper. However, there were no noticeable effects on extreme pressure characteristics. Nevertheless, when used in combinations with dibutyl phosphite and/or 2,5-dimercapto-1,3,4-thiadiazol, significant improvements in load – wear indices were shown. Although these were followed by decreased antioxidant activities, in all cases, their oxidation stabilities were still much better than those of the base case oil. In addition to gave an acceptable extreme pressure characteristics, the combination with 2,5-dimercapto-1,3,4-thiadiazol also showed a better rust/corrosion preventive characteristic. This revealed the possibility towards a lower or even zero phosphorus formulation.

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