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A Review on Addition of Molybdenum Compounds into Zinc Induced Bio-Lubricants as Lubricant Substitution

Muhamad Azwar Azhari, Lokman Hakim Mat, Mohd Farizzul Hakim Mohd Saroji,
Aliff Amirudin Mokhtaza and M. Hafiz Harun
Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia

Abstract: The needs of having an alternative lubricant to substitute mineral based lubricants caused the limelight to shift on vegetable oil. The decision on having vegetable oil as lubricant base stock is due to its bio-degradability and renewability apart from having good lubricant properties. However, the problem arises when vegetable oil based lubricants are prone to oxidation causing the lubricity and other physical properties to decrease. This study produces the review on addition of secondary antioxidant using zinc and molybdenum substances in order to reduce peroxide developed during propagation process during oxidation. From the review, it is proposed that a further experimental study to be conducted on vegetable oil based lubricants to examine the feasibility of introduction of molybdenum substances in zinc induced bio-lubricants.

Key words: Bio-lubricants, anti-oxidant, molybdenum, limelight, base stock

INTRODUCTION

For many years, mineral based oil lubricants were used to lubricate two moving contacting surfaces. Petroleum is the main source in producing mineral based oil lubricants. With the characteristics of non-renewable and non-biodegradable, concerns are raised towards the world resource and energy in the long-term. According to Mobarak *et al*. (2014) crude oil reserves in the world are facing depletion while the oil prices increase and the demand to oppose the pollution toward the environment caused by lubricating oils have prompted to development of an alternative lubricant. The facts that vegetable oil and most esters are bio-degradable compared to mineral oils have turned the attention of the world towards using vegetable oil as the base stocks in lubricant production. The possibility of vegetable oil replacing the mineral oil has been researched continuously. Regarding to the stated issue, this study reports the review of creating a new renewable and bio-degradable lubricant with the introduction of molybdenum compound into zinc induced vegetable oil as alternative to mineral based oil lubricants. Vegetable oils are known as a renewable resource and gaining their place into automotive applications and industrial lubricants. Due to its nontoxic nature, vegetable oil-based products have less concern with the environment especially issues pertaining to disposal of used oil (Srivasta and Sahai). Besides that, the other positive points that vegetable oil possess includes higher flash and fire points, high lubricity and high biodegradability (Azhari *et al*., 2014). A study by Mahipal *et al*. (2014) stated that vegetable oil have high value viscosity index due to high molecular weight of the triacylglycerol molecule resulting in low volatility and a narrow range of viscosity changes with temperature. These advantages make vegetable oil a very good candidate as an alternative to mineral based oil as lubricants. In contrast, the natural form of vegetable oil has some disadvantages with regards to its properties because of insufficient oxidative stability as lubricant.

According to Azhari *et al*. (2014) one of the problems in creating lubricants using vegetable oils is oxidation stability because of the higher content of unsaturated fatty acids causing the oil to be less cooperative in stabilizing oxidation process. With the increase in number of double bonds existed in fatty acids will lead to the increase on the level of unsaturation thus increasing the rate of oxidation (Azhari *et al*., 2006a, b). As a result, the oil if not treated will quickly oxidize, become thick and polymerize to a plastic-like consistency (Mobarak *et al*., 2014). As such, to improve the properties of vegetable oil, modification or addition of antioxidant could be done to stabilize the oxidation process (Azhari *et al*., 2014).

Corresponding Author: Muhamad Azwar Azhari, Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia

Table 1: Lubricating oil oxidation process (Azhari *et al*., 2014)

Steps	Equations
Initiation	RH • R• + H•
	R• + O_2 • ROO•
Propagation	ROO• + RH • ROOH + R•
	ROOH • RO• + •OH
Branching	RO• + RH • ROH + R•
	•OH + RH • H_2O + R•
Termination	R• + R• • R-R

VEGETABLE OIL OXIDATION

Generally, vegetable oils consist of aliphatic hydrocarbon chains with combination of saturated and unsaturated fatty acids. The unsaturated fatty acids are defined by the existence of double bond or bonds along the aliphatic chains (Kostik *et al*., 2013). These types of hydrocarbons are easily oxidized to form fatty acids, fatty aldehydes and ketones, fatty alcohols, fatty peroxides and fatty esters due to exposure to high temperature. A study by Azhari *et al*. (2014) suggested four primary steps in lubricating oil oxidation process which is initiations, propagation, branching and termination. The chemical equation for each steps are as depicted in Table 1. In initiation stage, the carbon and hydrogen bonds will be broken due to the existence of oxygen in the environment. During which organic species produces free radical (unpaired electron) where this active free radical will simply react with atmospheric oxygen and then forming a peroxy radical as reaction of radical nature of oxygen molecule (Lubis *et al*., 2015). The next step is the propagation step whereby the peroxide radical will form more radicals through reaction with more components in the lubricant (Azhari *et al*., 2014). Branching step which falls out after is an autoxidation process of the fatty acid and it will produce an additional secondary products such as are ketones (RCOR) and aldehydes (RCHO) (Lubis *et al*., 2015). This oxidation process shall be suppressed as oxidation of oil shall increase the kinematic viscosity and acidity of the oil (Srivastava and Sahai, 2013). If vegetable oil is to be used as a lubricant, anti-oxidizing agent shall be added as additive as to prevent this auto-oxidation process.

ANTI-OXIDATION

Anti-oxidant acts as important additives into lubricant to minimize and delay the degradation of lubricant oxidative. The antioxidant works in two different ways namely: radical scavenging where the antioxidants react with the radicals radicals to prevent the propagation of free radical chain and peroxide inhibition whereby the antioxidants react with the peroxide molecules in order to prevent any formation of the peroxy radicals. A study by Azhari *et al*. (2014) stated that primary antioxidants or radical scavengers are commonly consists of hindered phenolics and aromatic amines. Free radicals will react with radical scavengers before degradation of oil occur. Besides, primary antioxidants will donate a hydrogen atom to react with alkyl radicals and/or peroxy radicals as to interrupt the radical chain mechanism of the auto-oxidation process. Thus, it will be stable radical in form of hydrocarbon and alkyl hydroperoxide. Secondary antioxidants also known as peroxide decomposers will react with peroxide generated during propagation process in oxidation before the peroxide react with oxygen (Azhari *et al*., 2014). A study by Ahmed stated that there is several effective antioxidants classes have been researched and use in engine oils, gear oils, turbine oils, compressor oils, grease, hydraulic fluids, transmission fluids and metal working fluids. In this study, the focus of suppression of oxidation is through the termination of peroxides. As such, chemical compounds containing zinc and molybdenum are proposed as these compounds are found to be peroxide decomposer which is able to suppress oxidation in lubricant oil.

Zinc based additives: Introduction of Zinc Dialkyldithiophosphate (ZDDP) into lubricant oil as anti-oxidation agent was made as early as in the 1930's where ZDDP is added into engine oil applications and since then it has become one of the most effective lubricant additives. Apart from acting as an excellent anti-oxidation agent, it also has the properties of high effective anti-wear, corrosion inhibitor and extreme pressure additive (Chang *et al*., 2011). The physical appearance of ZDDP is of gold colored liquids and is similar to heavy syrup in regards of thickness or viscosity (Mahdi *et al*., 2012). Comparing ZDDP with water, ZDDP is denser than water and is insoluble in water however is highly soluble in oil and also lighter weight hydrocarbons as example gasoline. The formation and the speed of ZDDP forming film played the important role in preventing wear. Even after years of research, the understanding of the mechanism of formation and action of ZDDP as anti-oxidation and anti-wear film is still being studied. A study by Chang *et al*. (2011) stated that the mechanism of ZDDP as anti-wear agent is by providing a solid protective film when it reacts with the metal surface and the reaction layer was form by following four step process; break in, physical or chemical adsorption, additive-surface reaction and reaction layer growth. Many researchers have started to investigate the tribological properties of vegetable oil blended with ZDDP as additive. Azhari *et al*. (2006b) reported the results of addition of ZDDP in vegetable oil as additive. From the study, it can be concluded that addition of ZDDP into canola oil and corn oil provide a lot of benefits such as better performance and can improve the physical properties vegetable oil as lubricants. The result of the tests showed that the addition of 2.0 w.t.% concentration of ZDDP provides better results in viscosity, wear scar diameter and coefficient of friction compared to the other concentrations. On the other hand, a study by Mahipal *et al.* (2014) on the tribological test upon Karanja oil with additive of ZDDP shows that the 2.0 w.t.% ZDDP additive gives the most desirable result of coefficient friction, wear scar diameter, viscosity index and flash point and fire point compared to the commercial SAE 20W40 oil. Prior study has proven that the addition of antioxidant is capable to resolve the problems of oxidative stability in vegetable oil. A study by Azhari *et al.* (2014) stated that Zinc Dialkyldithiophosphate (ZDDP) was known as effective antioxidant that acts as an additive into vegetable oil to resolve the oxidation problem. ZDDP is considered as the key component for modern engine oils because it only presents the small fraction in total engine oil. It also can provide the wear protection of key metal-metal contact points and prolongs the life of transmission and engines (Mahdi *et al.*, 2012). Apart from zinc based additives, there is also molybdenum that could be added into lubricant oil as additive to prevent oxidation and improvement of physical property.

Molybdenum based additives: Molybdenum Dialkyldithiocarbamate (MODTC) act as an additive and is believed that it could reduce wear and friction in the boundary lubrication thus can promote fuel economy in engine oil because of it is capability to form the formation of tribofilms consist of molybdenum disulphide (MoS_2) and other molybdenum oxides (Yan *et al.*, 2012). Decomposition of MODTC produced the sheets MoS_2 and it is an excellent anti-friction agent because it easily brakes its bond (Liskiewicz *et al.*, 2013). Moreover, the modern study shows MoS_2 formation is focused on the MODTC concentration and rubbing process and not depends on the substrate properties. MoS_2 formation lean more towards pure sliding conditions compared to sliding or rolling conditions. When producing the low friction condition, the amounts of molybdenum containing additives depends on the formation of MoS_2 at asperity contacts (Komvopoulos *et al.*, 2006) Molybdenum containing compounds has proven as modifier additives for engine oils through formation of decomposition of MoS_2 which is done by complex tribochemical reaction to reduce friction (Komvopoulos *et al.*, 2006). The lamellar crystal structure of MoS_2 making it good in lubricating. When a force is applied normal to the lamellar crystal structure, the strong covalent bondings between molybdenum and sulfur atoms provide penetration resistance. Besides, molybdenum containing compounds need to be used at elevated temperature and high concentrations to act better as friction modifiers (Komvopoulos *et al.*, 2006). In contrast, molybdenum organic compound cannot improve the efficiency and performance on its own without any additional additives because maximum capability of molybdenum organic compound depends on the other additives (Komvopoulos *et al.*, 2006). The blended oil between of MODTC and ZDDP formed an anti-wear tribofilms consist of glassy zinc phosphate and carbon matrix containing of zinc sulfide and molybdenum disulphide. However, there will be a competition between the molybdenum compound and ZDDP to react with sliding surfaces and it can affect the chemical composition of the tribofilm, wear behaviour and friction (Komvopoulos *et al.*, 2006).

Zinc and Molybdenum Based Additives: A study by Xia stated that the high concentration of MODTC and ZDDP additive can form a uniform phosphate film and decomposition of MODTC which is MoS_2. This tribofilm formed in the wear scar influences in wear performance through friction reduction. MoS_2 film also acts as an improver in the durability of ZDDP. A research by Komvopoulos *et al.* (2006) concluded that ZDDP as an additive supports the formation of MoS_2 in the short chain of zinc polyphosphate. ZDDP also acts as the supplier of excess sulfur to complete the sulfuration of the molybdenum oxysulfide. The factors such as temperature, amount of elements of phosphorus and/or zinc and MODTC concentration, additional of other additives and structure influenced the coefficient of friction of MODTC. Results of tests reveal that it can reduce the coefficient of friction to a value as low as 0.05 (Liskiewicz *et al.*, 2013). Studies had shown that the mineral oil based lubricant formed containing ZDDP and MODTC can decrease the coefficient of friction and improve the wear resistance. A study by Tang and Li (2014) described that Molybdenum compounds, namely Molybdenum Dithiophosphate and Molybdenum Dithiocarbamate can be used independently in mineral based oil to reduce friction and wear. This is done by the formation of protective films containing Molybdenum compounds and Molybdenum oxides. However, a better anti-wear performance can be achieved when molybdenum compounds were added with Zinc Dilkyldithiophopsphate. Unnikrishnan *et al.* (2002) in their studies studied the effect of addition of Zinc Dialkyl dithio phosphate into Molybdenum Dithiocarbamate and Molybdenum Dithiophosphate as an anti-wear agent. From the results it is evident that the addition of Zinc Dialkyldithiophosphate improves the anti-wear properties of Molybdenum Dithiocarbamate and Molybdenum Dithiophosphate. The important role of surface rubbing to form anti-wear tribofilms is based on the higher concentration of zinc, molybdenum, sulfur and phosphorus on the wear tracks rather than unworn surfaces (Komvopoulos *et al*., 2006).

CONCLUSION

Zinc substance such as Zinc Dialkyldithiophosphate is known to be a very good anti-oxidation agent as well as anti-friction agent in mineral based lubricant oil. Previous research has shown that ZDDP is also compatible to be used as anti-oxidation and anti-wear additive in vegetable oil lubricants. As molybdenum has been studied and proven to be an improver to tribological properties of zinc induced mineral based lubricants, it is proposed that a study to be done upon the same additive on vegetable oil which can be proposed as an alternative to normal mineral based lubricant oil.

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REFERENCES

Azhari, M.A., Q.N. Suffian and N.R.M. Nuri, 2014. The effect of zinc dialkyldithiophosphate addition to corn oil in suppression of oxidation as enhancement for bio lubricants: A review. J. Eng. Appl. Sci., 9: 1447-1449.

Azhari, M.A.B., M.A. Fatheli, N.S.A. Aziz, M.S.M. Nadzri and Y. Yusuf, 2006a. A review on addition of zinc dialkyldithiophosphate in vegetable oil as physical properties improver. ARPN. J. Eng. Appl. Sci., 10: 6496-6500.

Azhari, M.A.B., M.F.B. Tamar and N.R.B.M. Nuri, 2006b. Physical property modification of vegetable oil as bio-lubricant using ZDDP. ARPN. J. Eng. Appl. Sci., 10: 6525-6528.

Chang, Z.Y., D.L. Breeden and M.J. McDonald, 2011. The use of zinc dialkyl dithiophosphate as a lubricant enhancer for drilling fluids particularly silicate-based drilling fluids. Proceedings of the SPE International Symposium on Oilfield Chemistry, April 11-13, 2011, Society of Petroleum Engineers, Oklahoma, USA., pp: 1-7.

Komvopoulos, K., S.A. Pernama, E.S. Yamaguchi and P.R. Ryason, 2006. Friction reduction and antiwear capacity of engine oil blends containing zinc dialkyl dithiophosphate and molybdenum-complex additives. Tribol. Trans., 49: 151-165.

Kostik, V., S. Memeti and B. Bauer, 2013. Fatty acid composition of edible oils and fats. J. Hygienic Eng. Des., 4: 112-116.

Liskiewicz, G., P. Kula, A. Neville, R. Pietrasik and A. Morina *et al*., 2013. Hydrogen influence on material interaction with ZDDP and MoDTC lubricant additives. Wear, 297: 966-971.

Lubis, A.M.H.S., B. Ariwahjoedi and M.B. Sudin, 2015. Investigation on oxidation of jatropha oil. Proc. Mechanical Eng. Res. Day, 2015: 53-54.

Mahdi, I., R. Garg and A. Srivastav, 2012. ZDDP-an inevitable lubricant additive for engine oils. Intl. J. Eng. Inventions, 1: 47-48.

Mahipal, D., P. Krishnanunni, P.M. Rafeekh and N.H. Jayadas, 2014. Analysis of lubrication properties of zinc-dialkyl-dithio-phosphate (ZDDP) additive on Karanja oil (*Pongamia pinnatta*) as a green lubricant. Intl. J. Eng. Res., 3: 494-496.

Mobarak, H.M., E.N. Mohamad, H.H. Masjuki, M.A. Kalam and K.A.H.A. Mahmud *et al*., 2014. The prospects of biolubricants as alternatives in automotive applications. Renewable Sustainable Energy Rev., 33: 34-43.

Srivastava, A. and P. Sahai, 2013. Vegetable oils as lube basestocks: A review. Afr. J. Biotechnol., 12: 880-891.

Tang, Z. and S. Li, 2014. A review of recent developments of friction modifiers for liquid lubricants (2007-present). Curr. Opin. Solid State Mater. Sci., 18: 119-139.

Unnikrishnan, R., M.C. Jain, A.K. Harinarayan and A.K. Mehta, 2002. Additive-additive interaction: An XPS study of the effect of ZDDP on the AW/EP characteristics of molybdenum based additives. Wear, 252: 240-249.