ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

THE EFFECT OF ZINC DIALKYLDITHIOPHOSPHATE ADDITION TO CORN OIL IN SUPPRESSION OF OXIDATION AS ENHANCEMENT FOR BIO LUBRICANTS: A REVIEW

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ABSTRACT

The needs of having a substitute for petroleum based lubricant are being studied by researchers since the last decades. Vegetable oil which is known to be biodegradable, renewable and have the similar properties of lubrication as petroleum based oil is seen to be a candidate for the substitution. However, the high content of unsaturated fatty acids in vegetable oils causes the oil to be less cooperative in stabilizing oxidation. The purpose of this paper is to discuss the effect of zinc dialkyldithiophosphate (ZDDP) addition as antioxidation agent in commercialized corn oil process as a barrier to commercialized corn oil. The introduction of ZDDP into the corn oil could resolve the oxidation problem since ZDDP is an effective antioxidant. The capability of ZDDP exhibits both primary and secondary antioxidant is desirable in biolubricant oil in order to suppress the oxidation process.

Keyword: bio lubricant, ZDDP, oxidation.

INTRODUCTION

Since 1650BC, vegetable oil has been widely used as lubricant. According to Gawrilow, (2003), olive oil was used as lubricant to lubricate machineries at that time. The introduction of new interest in biolubricant is due to increase in crude oil prices, depletion of crude oil reserves and growing environmental concerns.

The purpose of machinery lubrication is to avoid direct contact between the various rolling and sliding elements. This is accomplished through the formation of a thin oil film between the contacting surfaces. Lubrication has the following advantages: Reduction of friction and wear, dissipation of friction heat, prolonged bearing life, prevention of rust and protection against harmful elements [1].

There are numerous vegetable oils resulting from various parent oil. The popular biolubricant soybean, cottonseed, peanuts and sunflower oils; and others such as palm oil, palm kernel oil, coconut oil, castor oil, rapeseed oil and corn oil [2]. Vegetable oils have exhibited brilliant lubrication properties in laboratory studies. Composition and selected properties of vegetable oils commonly investigated as potential lubricants. Vegetable oils are composed of triglycerides of fatty acids, and have admirable qualities like enhanced flash and fire points, higher viscosity and viscosity index, high biodegradability, high lubricity, and very less toxicity. Vegetable oils are of two types, Edible and Non edible. Edible oil; A liquid fat that is accomplished of being eaten as a food or food access, like Coconut, Olive, Soyabean, Sunflower, Palm, Peanut, Rapeseed, Corn etc. Non edible; As a substitute non edible vegetable oil can prove to be valuable like Neem, castor, Mahua, rice bran, karanja, Jatropha, and linseed oils [3]. Fox and Stachowiak [4] reviewed that long, polar fatty acid chains provide high strength lubricant films that interact strongly with metallic surfaces, reducing both friction and wear. The strong intermolecular interactions are also resistant to changes in temperature providing a more stable viscosity, or high viscosity coefficient. The entire base oil is also a potential source of fatty acids.

Oxidation stability of vegetable oil is one of the problems in formulating the vegetable oils. The high content of unsaturated fatty acids in vegetable oils produces the oil less cooperative in stabilizing the oxidation. The modification of the vegetable oil or addition of antioxidant additives could help in stabilizing the oxidation process [5]. Characteristic drawbacks and the availability of inexpensive options have brought the low utilization of vegetable oils for industrial lubrication. Vegetable oil does not volatilize without decomposing. Their superior lubricity and emulsifying characteristics increase their desirability as additives to the cheaper but less effective mineral oil based lubricants. The benefits that inspire the use of vegetable oils include their relatively low viscosity-temperature variation; high viscosity stability, makes them twice of mineral oils. Vegetable oil oxidation is started by formation of free radicals which can be easily being formed from the removal of a hydrogen atom from the methylene group next to a double bond. The peroxy radicals are formed as free radicals rapidly react with oxygen. The peroxy radical can then attack another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical, propagating the oxidation process which is undesirable to most of industrial lubrication [6].

THEORY

Both oxygen content and exposure period give a significant factor in the formation of undesired compounds, which can corrode metals and cause the system to clog. Thus, oxidative stability has to be considered as an essential characteristic in the control of the biolubricant properties.

The process of oxidation arises by a three-step process; initiation, propagation and termination. During initiation stage, free radical (unpaired electron) is produced in organic species due to external factors. This process involves breaking a bond with a hydrogen atom.

In propagation step, it leads to further decomposition of the lubricant oil. This happens when free radical is a highly reactive species reacts with oxygen to form peroxide radical which can generate additional radicals through reaction with more components in the lubricant. A stable compound is formed when two of free radicals are combined together. This is designated as the termination step because it removes free radicals from the system. Table-1 shows the reaction equation of oxidation process.

Table-1. Autoxidation mechanism in three-step process [4].

Initiation	**RH → R• + H•**
Propagation	• R• + O_2 → ROO• • ROO• + RH → ROOH + R•
Branching	• ROOH → RO• + •OH • RO• + RH + O_2 → ROH + ROO• • •OH + RH + O_2 → H2O + ROO•
Termination	• ROO• + ROO• → ROOH + O_2 • ROO• + R• → ROOH • R•+R•→ R-R

By checking the level of acidity and the increment of viscosity with oxidation, the oxidation stability can be measured. Lubricating oils are vulnerable to degradation by oxygen. The oil oxidation process is the main reason of oil thickening [7], [8] and [9]. This consequence in the formation of sludge and varnish on engine parts, causing increased engine wear, poor lubrication, and reduced fuel economy. Antioxidants are vital additives merged into lubricant formulations to decrease and delay the onset of lubricant oxidative degradation.

In order to extend the life of oil, the addition of antioxidant increases the oxidative resistance. There are two types of antioxidants: primary and secondary antioxidants. Primary antioxidants are typically covered of aromatic amines and hindered phenolics. Secondary antioxidants are typically encompassed of phosphites and certain sulfurcontaining compounds, such as thioethers and thioesters. Each type of antioxidant completes a different function to inhibit oxidation. Primary antioxidants are “radical scavengers” that react quickly with the free radicals that form before they can cause degradation of the oil. Secondary antioxidants react with peroxides which are often present as the lubricating oil reacts with oxygen. Most often, grease formulators will use a combination of antioxidants to maximize the protection of the oil against oxidative degradation [10].

CASE STUDY

The main factors of initiation of oxidation process are temperature, metal traces, oxygen and unsatured fatty acid. Corn oil, as a parent vegetable oil, is vulnerable to oxidation because of its unsaturated fatty acid content [2]. The low oxidation stability of all kind of vegetable oils is due to their unsaturated double bonds in the fatty acids and is said to be active sites for many reactions, including oxidation. The greater the level of unsaturation, that is, the more double bonds, the more susceptible the oil becomes to oxidation [4].

There are some of drawbacks of using vegetable oil lubricant. Due to low thermal and oxidation stability, there is a limitation for vegetable oil to be used in industrial field. This is the biggest problem carried by vegetable oil in order to make them as a lubricant. This situation leads to a better understanding of the oxidation process of prospective bio-based lubricants and their blend with antioxidant additives is required.

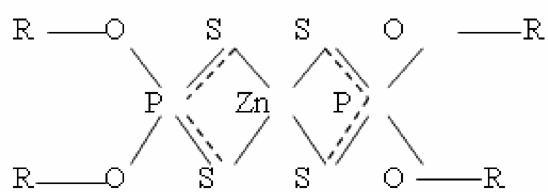

Figure-1. The structure of zinc dithiophosphate. The R group describes whether it is an alky- or aryl-dithiophosphate [12].

The introduction to antioxidant additive (ZDDP) into the vegetable oil can resolve the problem stated since ZDDP is an effective antioxidant known. A few sample tests will be carried out to test the effectiveness of the ZDDP in the vegetable oil (corn oil). It is believe that the presence of sulphide in the ZDDP, the initiation of new radical chains is decelerated. Hydroperoxide decomposers include sulfides react with hydroperoxides producing alcohols and sulfoxides. Sulfoxides can react further and remove additional equivalents of hydroperoxides in a complicated series of reactions. Thus, the oxidation process can be slowed down [11].

The existence antiwear chemistry was made during the 1930s and 1940s with the discovery of zinc dialkyldithiophosphates (ZDDP) [7]. The primary function of ZDDP to prevent bearing corrosion but were later found to have exceptional antioxidant and antiwear properties. The antioxidant mechanism of the ZDDP was the key to its ability to reduce bearing corrosion, since the ZDDP suppresses the formation of peroxides. Antiwear and extreme-pressure additives function by thermally decomposing to yield compounds that react with the metal surface. These surface-active compounds form a thin layer that preferentially shears under boundary lubrication conditions.

The introduction of ZDDP upon corn oil can bring the oxidation stability of the oil to the maximum level. The capability of ZDDP exhibits both primary and secondary antioxidant is desirable in biolubricant oil in order to suppress the oxidation process. Allyson, Keith and Vincent [13] reviewed that it is difficult to understand the mechanisms of degradation of ZDDP.

Brazier and Elliot [14] investigated the thermal decomposition of ZDDPs and reported that most ZDDPs decompose in two stages. The thermal stabilities of ZDDPs derived from straight chain primary alcohols were seen to increase with increasing carbon number. Burn *et al*. [15] studied the additive of ZDDP with decomposition of cumene hydroperoxide (CHP). Although a definitive mechanism of degradation of ZDDP could not be produced, the three stages of breakdown were hypothesized. The authors detected an initial fast stage; disulphide was identified as initial product of degradation. This reaction was then followed by slow induction stage to a final last stage. Based on the review of others researchers, the presence of ZDDP in corn oil can slow down the oxidation of the oil.

CONCLUSIONS

The behaviour of ZDDP, although its degradation mechanism is not clearly reviewed, from most of the researcher, it is found that ZDDP gives a positive potential towards the suppression of oxidation process. The evaluation of corn oil and ZDDP has been made and it is expected that antioxidizing agent, ZDDP will help enhance the oxidation stability in the corn oil as a primary and secondary antioxidant.

ACKNOWLEDGEMENT

The author would like to acknowledge the Ministry of Science Technology and Innovation and Universiti Teknikal Malaysia Melaka for the support and funding throughout these studies.

REFERENCES

[1] J. Zhu, J. M. Yoon, D. He, Y. Qu and E. Bechhoefer. 2013. Lubrication Oil Condition Monitoring and Remaining Useful Life Prediction with Particle Filtering. *International Journal of Prognostics and Health Management*. 20: 1-15.

[2] E. O. Aluyor and M. Ori-Jesu. 2008. The use of antioxidants in vegetable oils - A review. *African Journal of Biotechnology*. 7(25): 4836-4842.

[3] Sevim, Z. Erhan, Brajendra, K. Sharma, Joseph, M. Perez. 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. Industrial Crops and Products. 24: 292-299.

[4] Fox N.J. and Stachowiak G.W. 2007. Vegetable oil-based lubricants-A review of oxidation. Tribology International. 40: 1035-1047.

[5] Masabumi M., Hiroyasu S., Akihito S. and Osamu K. 2008. Prevention of oxidative degradation of ZnDTP by micro capsulation and verification of its antiwear performance; Tribology International. 41, 1097-1102.

[6] M. Dantas, A. Albuquerque, A. Barros, M. Rodrigues Filho, N. Antoniosi Filho, F. Sinfrônio, R. Rosenhaim, L. Soledade, I. Santos and A. Souza. 2010. Evaluation of the Oxidative Stability of Corn Biodiesel. Fuel 90, 90: 773-778.

[7] Ludema K.C. 1996. Friction, Wear, Lubrication, A Textbook in Tribology, CRC Press L.L.C., 124- 134.

[8] Leslie R.R. 2003. Lubricant Additives. Chemistry and Applications. Marcel Dekker, Inc. 293-254.

[9] Rizvi, S.Q.A. 2009. A comprehensive review of lubricant chemistry, technology, selection, and design. ASTM International, West Conshohocken, PA., 100-112.

[10] N. S. Ahmed and A. M. Nassar. 2011. Lubricating Oil Additives. In Tribology - Lubricants and Lubrication, Egypt, In. Tech. pp. 249-268.

[11] B. Grigor B., B. Girma, M. Abdellatif and M. Jill. 2010. Temperature dependence of the oxidative stability of corn oil and polyalphaolefin in the presence of sulfides. Thermochimica Acta. 513: 94-99.

[12] S. A. Watson. 2010. Lubricant Derived Ash in Engine Sources and Opportunities for Reduction. Massachussets: Massachussets Institute of Technology.

[13] A. M. Barnes, K. D. Bartle and V. R. Thibon. 2001. A review of zinc dialkyldithiophosphates (ZDDPS): Characterisation and role in the lubricating oil. Tribology International. 34: 389-395.

[14] Brazier AD, Elliott JS. 1967. The thermal stability of zinc dithiophosphates. J Inst Petrol. 53(518): 63-76.

[15] Burn AJ, Cecil R, Young VO. 1971. Peroxide-decomposing antioxidants. Mechansims of the decomposition of cumene hydroperoxide in the presence of zinc diisopropyldithiophosphate. J Inst Petrol. 57(558): 319-30.