

An alternate to Dithiophosphate Additives to Lubricants:

Eco Friendly Lubricants

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ABSTRACT

The tribological perspectives of dithiophosphate based lubricant additives has been known since a long time. The hazardous effects caused by them are the matter of recent research as a lot of damage has been caused to the environment due to the application of such lubricants on large commercial level. The desirability of novel bio-based lubricants began with vegetable oils due to their low friction and wear properties. The tribological characteristics are perhaps superior due to the presence of triacylglycerol molecules made up of esters derived from glycerol and long chains of polar fatty acids as the basic chemical composition. The fatty acids within the natural oils are the main contributors of high lubricity of that establish monolayers that. However, these vegetable oils suffer from thermal-oxidative instability, high pour points and inconsistent chemical compositions. Presently, lubricants derived from natural resources exhibit a promising potential as a new class of eco-friendly lubricants.

Keywords – Dithiophosphate, Lamellar additives, Lubricants, Natural oils, Tribology.

I. INTRODUCTION

A lubricant is a substance introduced between two moving surfaces to reduce friction, reduce wear, eliminate contaminants, distribute heat, and improve efficiency. To understand the importance of the role played by lubricants in our life we need to survey the many macroscale applications that utilize lubricants such as internal combustion engines, turbines, hydraulic systems, compressors, vehicle and industrial gearboxes and journal and thrust bearings as well as the various micro- and nanoscale applications and metal forming applications[1-3]. From ancient times the biolubricants derived from plant oils and animal fats are being used. Scientists have recognized that biolubricants provide favorable friction and wear properties. Since the beginning of the twentieth century, exploration of the properties of bio-based oils have received considerable attention due to the fact that 50 % of all lubricants worldwide end up in the environment through usage, spill, volatility or improper disposal [4-6]. Petroleum-based oils form 95 % of these lubricants that enter into the environment and are injurious to many biological ecosystems [7]. The introduction of petroleum-based oils in the mid-1800s, led to dramatic decline in the use of bio-based oils as lubricants. Resurgence of eco-friendly lubricants has begun as a result of increased environmental efforts to reduce the use of petroleum-based lubricants in addition to the exhaustion of oil reserves, increase in oil price and rises in lubricant disposal expenses [8,9].

II. ENVIRONMENTAL IMPACT OF LUBRICANTS

The release of used oil to the environment, by accident or any other reason is threatening to the ground soil and surface waters with oil contamination thereby jeopardizing drinking water supply and aquatic organisms. It has been established that used oil can damage the environment in several different ways. Spilled oil tends to accumulate in the environment, causing soil and water pollution. Oil decomposition is very slow. It reduces the oxygen supply to the microorganisms that breakdown oil into non-hazardous compounds. Toxic gases and harmful metallic dust particles are produced by the combustion of used oil. The high concentration of metal ions, lead, zinc, chromium and copper in used oil can be toxic to ecological systems and to human health if they are emitted from the exhaust of uncontrolled furnaces. Phosphorus based additives like zinc dialkyldithiophosphates contaminate the environment[10]. Other contaminants include antifreeze/coolant, water, wear metals, metal oxides and combustion products. The important cause of soil biodiversity loss in urban areas is the pollution of soils by petroleum products. Waste engine oil results in contamination by chemical impurities that lead to chronic hazards including mutagenicity and carcinogenicity. Waste engine oil is a mixture of several different chemicals including low and high molecular weight aliphatic hydrocarbons, aromatic hydrocarbons, polychlorinated biphenyls, chloro dibenzofurans, lubricative additives, decomposition products and heavy metal contaminants such as aluminum, chromium, lead, manganese, nickel and silicon that come from engine parts as they wear down. Such contamination results in habitat transformation indicated by the absence of myriapod species and decrease in population of other arthropods at the contaminated sites. This results in biodiversity loss and elimination of species in the habitat[11].

III. TOXICITY ANALYSIS OF ADDITIVES

The relative substance toxicity of lubricants is analyzed to classify additives worldwide. This study is based on the fact that how the additives adversely affect the representative aquatic test organisms (fish, aquatic invertebrates, and algae) when they are directly added to the test water. The test organisms are exposed to different fractions of the additive- the water-soluble portion, portions that form dispersions or emulsions and the insoluble fraction which lies on the surface of the water. Therefore, the effects observed on the organisms could be influenced by the non-soluble fractions of the material which may cause fouling that may interfere with the observation of toxic effects and can be evaluated by reviewing the physical/chemical properties of the lubricant additives. Such various experiments have proven that the lubricant additives are practically non-toxic to aquatic test organisms, except for ZDTPs and hindered phenolics. The EC50 is defined as the concentration of material that would affect 50 % of the test organisms during the exposure period. The greater the EC50 value the lower the toxicity of the material[12,13].

'Active' sulfur content of sulfur containing additives is estimated by the tendency of sulfur to react chemically at low temperatures. High active sulfur content is desirable when low temperature performance is required but this can also lead to corrosion, particularly of copper. Zinc dialkyldithiophosphates (ZDTPs) are the widely accepted multifunctional additives. They act as anti-oxidants, anti-wear agents and corrosion inhibitors. ZDTPs are made by the reaction of alcohols, phosphorus pentasulphide (P_2S_5) and zinc oxide. Alcohol used to make a ZDTP varies from primary ethanol, propanol to higher aryl analogues such as aryl alcohols[14,15]. Low molecular weight (three to six carbon atoms) secondary alcohols are used to prepare ZDTPs for use in

automotive lubricants. Decomposition of these additives at low temperatures makes them proficient as wear inhibitors. Industrial oil applications use ZDTPs made from primary (four to eight carbon atoms) alcohols which exhibit superior oxidative performance comparative to secondary ZDTPs. The major human health hazard of concern with ZDTPs is their eye irritation potential and mutagenic nature in chronic cases.

IV. INCLINATION TOWARDS BIO-BASED LUBRICANTS

Due to several hazards caused by the petroleum-based lubricants such as toxic effects in environment and renewability there has been sharp inclination towards the bio-based natural lubricants in the recent decade. Bio-based lubricants have a higher lubricity, lower volatility, higher shear stability, higher viscosity index, higher load carrying capacity and superior detergency and ability to disperse to greater extent [16,17]. Conventional eco-friendly lubricants are usually derived from natural sources like plants and certain animals and therefore their availability and properties are based on biological factors such as nutrient availability, climate, light, temperature and water [18,19]. Latest eco-friendly lubricants are being used as carrier fluids for lamellar powder additives in sliding contact [20,21]. Lamellar powder additives in eco-friendly lubricants consist of nontoxic lamellar powders such as boric acid (H_3BO_3) and boron nitride (BN) These enable reduced friction, form protective boundary layers, and accommodate relative surface velocities [16,21]. The atoms of such additives form layers through strong covalent bonds that are held together through the weak van der Waals forces providing the minimal shear resistance and enabling the low interlayer friction [22]. These lamellar powders have established themselves as a success in a broad range of environments of extreme pressure and temperature and have made their place in various applications from automotive to aerospace to lower friction and minimize wear [19].

It seems obvious that these bio lubricants are already available for the majority of applications and that the technical performance is comparable or even superior to conventional lubricants. The amplified utilization of rapidly biodegradable lubricants would be of considerable ecological and economical advantage as they display exceptional tribological properties, lower friction coefficients than mineral-oil-based fluids, lower evaporation, higher viscosity index, excellent biodegradability, high flashpoints and low water pollution classification. Their technical properties are thus basically comparable with mineral-oil-based fluids. Henceforth, technical performance, acceptable price and ecological compatibility will constitute the basis for future developments along these lines.

V. DRAWBACKS OF BIO-BASED LUBRICANTS

In spite of the great benefits of bio-based lubricants over petroleum-based lubricants that exhibit environmental hazards with global ramifications, they have not yet envisaged the entire lubricant industry. The reasons for such a scenario are low thermal stability than mineral oils, sensitivity to hydrolysis and oxidative attack, high pour points, inconsistent chemical composition, hydrolytic instability, severe susceptibility to biological deterioration, insufficient low-temperature behavior. Utilizing the renewable resources such as native plant oils as the lubricants and hydraulic fluids, a compromise between the performance based on the chemical structure and the desired biodegradability and eco-toxicity has to be made. On the other hand, lamellar powders suffer from concentration optimization and therefore, high costs, unwanted abrasive behavior due to particle size and

shape, large particles can block tubes within critical engine parts, and they can clog oil filters in circulatory lubrication systems. These limitations of traditional eco-friendly lubricants in due course cause economic issues where the lubricants can become very expensive when their properties are transformed for larger variety of potential applications.

VI. CONCLUSION

Prospective of the lubrication industry seems to be introduction of new technology that meets the human health and eco-toxicity requirements. Special consideration is being given to bio-accumulation and biodegradation of lubricants in the environment. The new technology may create sustainable eco-friendly lubricants with properties that will lower friction and wear, thereby improving system efficiency ultimately conserving energy, a higher lubricity leading to lower friction losses and improved efficiency, affording more power output and better economy. With increasing oil prices and environmental awareness, the demand for renewable and sustainable lubricants increases. Funding of fundamental research is being improved to augment the macroscale development, economical competence, and industrial use of biolubricants for energy conservation and sustainability.

REFERENCES

- [1.] C. Reeves, P.L. Menezes, M. Lovell and T-C. Jen, Macroscale applications in tribology. In: P.L. Menezes, M. Nosonovsky, S.P. Ingole, S.V. Kailas, M.R. Lovell (eds) *Tribology for scientists and engineers*. Springer, New York, 2013, 881–919
- [2.] C. Reeves, P.L. Menezes, M. Lovell and T-C. Jen, Microscale applications in tribology. In: P.L. Menezes, M. Nosonovsky, S.P. Ingole, S.V. Kailas, M.R. Lovell (eds) *Tribology for scientists and engineers*. Springer, New York, 2013, 921–948
- [3.] P.L. Menezes, C. Reeves, S.V. Kailas and M. Lovell, Tribology in metal forming. In: P.L. Menezes, M. Nosonovsky, S.P. Ingole, S.V. Kailas, M.R. Lovell (eds) *Tribology for scientists and engineers*. Springer, New York, 2013, 783–818
- [4.] S.M. Lundgren, K. Persson, G. Mueller, B. Kronberg, J. Clarke, M. Chtaib et al, Unsaturated fatty acids in alkane solution: adsorption to steel surfaces. *Langmuir ACS J Surf Colloids*, 23, 2007, 10598–10602
- [5.] M.R. Lovell, P.L. Menezes, M.A. Kabir and C.F. Higgs III, Influence of boric acid additive size on green lubricant performance. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, 368, 2010, 4851–4868
- [6.] S.M. Lundgren, M. Ruths, K. Danerlov and K. Persson, Effects of unsaturation on film structure and friction of fatty acids in a model base oil. *J. Colloid Interf. Sci.*, 326, 2008, 530–536.
- [7.] M.P. Schneider, Plant-oil-based lubricants and hydraulic fluids. *J. Sci. Food Agric.*, 86, 2006, 1769–1780.
- [8.] K.S. Deffeyes, *Hubbert's peak*. Princeton (N.J.). Princeton University Press, Oxford, 2009.
- [9.] D.L. Goodstein, *Out of gas: the end of the age of oil*, 1st edn. W.W. Norton, New York, 2004.
- [10.] C. M. Cisson, G. A. Rausina and P. M. Stonebraker, Human health and environmental hazard characterisation of lubricating oil additives, *Lubrication Science*, 8(2), 1996, 145–177.
- [11.] J. Rotimi and O.A. Ekperusi, Effect of spent lubricating oil on the composition and abundance of arthropod communities of an urban soil, *J. Sci. Env. Manage.* 18(3), 2014, 411–416.

- [12.] A. Willing, Lubricants based on renewable resources-an environmentally compatible alternative to mineral oil products, *Chemosphere*, 43, 2001, 89-98.
- [13.] E. Jorgensen, *Ecotoxicology*, Academic Press, 2010.
- [14.] S. Kour, B. Gupta, R. Chander and S. K. Pandey, *O,O'*-Ditolylidithiophosphates of zinc(II), cadmium(II) and mercury(II), *Main Group Metal Chemistry*, 32(4), 2009, 195.
- [15.] M. S. Saini, A. Kumar, O. Singh and J. Dwivedi, Synthesis and Characterization of New Complexes *O, O'*-Bis(A-Naphthyl, B-Naphthyl and 2, 3, 5- Trimethylphenyl)Dithiophosphate of Zinc (II), Cadmium (II) And Mercury (II), *Inter. J. Sci. Nature*, 4(2), 2013, 299-303.
- [16.] P.L. Menezes, M.R. Lovell, M.A. Kabir, C.F. Higgs III and P.K. Rohatgi, Green lubricants: role of additive size. In: Nosonovsky M, Bhushan B (eds) *Green tribology*. Springer, Berlin, 2012, 265–286.
- [17.] M. Bennion and B. Scheule, *Introductory foods*. Prentice Hall, Upper Saddle River, 2010.
- [18.] H. Duzcukoglu and O. Sahin, Investigation of wear performance of canola oil containing boric acid under boundary friction condition. *Tribol. Trans.* 54, 2011, 57–61
- [19.] M. Lovell, C.F. Higgs, P. Deshmukh and A. Mobley, Increasing formability in sheet metal stamping operations using environmentally friendly lubricants. *J. Mater. Process. Technol.* 177, 2006, 87.
- [20.] J. Grushcow and M.A. Smith, Next generation feedstocks from new frontiers in oilseed engineering. *ASME Conf. Proc.*, 2005, 487–488.
- [21.] C.J. Reeves, P.L. Menezes, M.R. Lovell and T-C Jen, The size effect of boron nitride particles on the tribological performance of biolubricants for energy conservation and sustainability. *Tribol. Lett.* 51, 2013, 437–452.
- [22.] C. Reeves, P.L. Menezes, M. Lovell and T-C Jen, Tribology of solid lubricants. In: Menezes PL, Nosonovsky M, Ingole SP, Kailas SV, Lovell MR (eds) *Tribology for scientists and engineers*. Springer, New York, 2013, 447–494.