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RESEARCH

# Enhanced Biodegradability, Lubricity and Corrosiveness of Lubricating Oil by Oleic Acid Diethanolamide Phosphate

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A B S T R A C T

*Impacts of oleic acid diethanolamide phosphate (abbreviated as ODAP) as an additive on biodegradability, anti-wear capacity, friction-reducing ability and corrosiveness of an unreadily biodegradable HVI 350 mineral lubricating oil was studied. The biodegradabilities of neat lubricating oil and its formulations with ODAP were evaluated on a biodegradation tester. Furthermore, the anti-wear and friction-reducing abilities and the corrosiveness of neat oil and the formulated oils were determined on a four-ball tribotester and a copper strip corrosion tester, respectively. The results indicated that ODAP markedly enhanced biodegradability as well as anti-wear and friction-reducing abilities of the lubricating oil. On the other hand, excellent color ratings of copper strips for both neat oil and the ODAP-doped oil were obtained in the corrosion tests, demonstrating that the corrosiveness of neat oil and the doped oil was negligible, although the latter seemed to provide slightly better anti-corrosion ability.*



## 1. INTRODUCTION

It has been known that environmental pollution caused by petroleum-based lubricants is severe due to their inherent toxicity and non-biodegradable nature [1-2]. During the last decades, the increased public attention and the awareness of protection of the environment have stimulated the development of lubricants that show more or less compatibility with the environment, and environmental compliance of lubricants has become a topic of interested research [3-6]. As we know, the key issue in formulating biodegradable lubricants is the choice of reliable base oils and suitable performance additives. Nowadays, many base fluids such as vegetable oils and synthetic esters have found practical applications in the formulation of biodegradable lubricants because of their excellent biodegradability and non-toxicity [7-9]. On the other hand, the development of alternatives to conventional lubricant additives such as ZDDP has also been a subject of significant interest, mainly due to environmental concerns arising from S, P and metal atoms of the additives [10]. As we know, petroleum-based lubricants, which consist predominantly of hydrocarbons and subsidiarily of additives which are often environmentally hazardous, for many reasons still dominates the lubricant market and will presumably continue to play their important roles in the future lubrication applications. Even though choice of mineral base oils in biodegradable lubricant formulations has as far never been recommended, improvement of their environmental safety such as better biodegradability and development of greener additives are indeed indispensable.

Fatty acid alkanolamide phosphates have been known to be effective anionic surfactants providing excellent detergency, wetting ability, emulsifying capacity, rust-inhibiting property, and so on, and have been widely used in many fields such as textiles, pesticides and cosmetics. In addition, fatty acid alkanolamide phosphates are phosphorous and nitrogenous compounds. They may function as nutriments for microbes and, if incorporated into an unreadily biodegradable lubricant, are expected to be capable of promoting microbial production, thus improving biodegradability of the lubricant. Indeed, some phosphorous and nitrogenous compounds have been proven to be effective in enhancing biodegradability of mineral lubricating oils [11]. Furthermore, organic phosphates such as tricresol phosphate have been well known boundary lubrication additives for lubricants. It can therefore be inferred that, when incorporated into a lubricant, polar fatty acid alkanolamide phosphates may adsorb on or react with tribomates to act as friction and wear reducers, fortifying anti-wear and friction-reducing abilities of the lubricant in tribological processes as a result. In the present paper, the effects of oleic acid diethanolamide phosphate on biodegradability, anti-wear and friction-reducing abilities, as well as anti-corrosiveness, of a mineral lubricating oil were investigated.

## 2. EXPERIMENTALS

### 2.1 Materials

HVI 350 Lubricating oil: Well refined petroleum-based paraffinic lubricating base oil whose kinematic viscosity at 40 °C is 68.76 mm2/s.

Oleic acid diethanolamide phosphate (abbreviated as ODAP): A redish-brown greasy compound prepared by the authors by reacting oleic acid with diethanolamine and phosphorus pentoxide, respectively, under catalyst, and purified under vacuum distillation. The preparation and characterization of ODAP were specified in the reference [12].

Oleic acid: A chemically purified, readily biodegradable unsaturated fatty acid, used as a reference substance in the biodegradation test.

### 2.2. Biodegradation test

For evaluating the effect of ODAP on biodegradability of lubricating oils, different mass percentage of ODAP, viz. 0.0%, 0.5%, 1.0% and 1.5%, were incorporated into HVI 350 mineral lubricating oil. The biodegradabilities of neat oil and the formulated oils were evaluated by means of a fast method for determining biodegradability of lubricants created by the authors, the principle of which was based on the determination and comparison of carbon dioxide produced by a tested lubricant and a reference substance after biodegradation reaction. The inoculum used in the biodegradation test was indigenous microbes in the sewage obtained from an urban wastewater treatment plant. The active microbe populations were $7.8\times10^7$ CFU per mililiter of the sewage. The test conditions and operation processes of this method were specified in the reference [13]. In short, determination of biodegradability of a lubricant by this method is conducted by parallel biodegradation reactions of the lubricant and the reference substance oleic acid. After a period of biodegradation under the formulated conditions, the accumulated amount of carbon dioxide produced by the tested lubricant and oleic acid were measured, respectively. Biodegradability index (BDI), a comparative parameter of the percentage ratio of the amount of $CO_2$ created by the tested lubricant to that created by oleic acid, was calculated to evaluate the biodegradability of the lubricant. The higher the BDI value, the better the biodegradability of a lubricant. The method has been proven to be well correlated with the prevailing biodegradation test method of CEC-L-33-A-94. Fig. 1 shows the schematic diagram of our method.

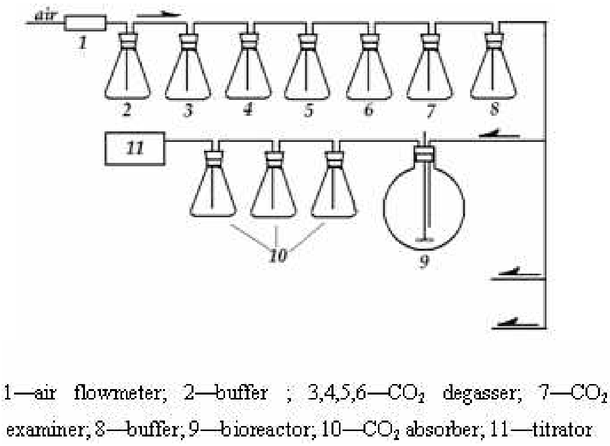


**Fig. 1.** Schematic diagram of biodegradation test.

### 2.3 Friction and wear test

The anti-wear and friction-reducing abilities of ODAP-doped lubricants were evaluated on a four-ball tribotester following the GB/T 3142 procedures, a Chinese standard method for determining load carrying capacity of a lubricant which well corresponds to the ASTM D2783 and ASTM D4172. The four-ball tester consists of a rotating ball that glides under selected loads on three fixed balls. The load is exerted on the rotating ball and increased at defined steps. In the present test, the maximum non-seizure loads ($P_B$), welding loads ($P_D$), wear scar diameters (WSD) and friction coefficients, which well characterize the friction and wear behaviors of a lubricant in the four-ball testing, were determined under the rotary speed of 1500 r/min at room temperatures. The duration in determining $P_B$ and $P_D$ at each load was ten seconds. The WSD and friction coefficient were tested under the loads of 392N for 30 minutes. The higher the $P_B$ and $P_D$, and the lower the WSD and friction coefficient, the better the lubricating property of a lubricant. The balls used in the present test are GCr15 bearing steel balls 12.7 mm in diameter, 59 ~ 61 HRC in hardness and Ra 0.040 μm in surface roughness.

### 2.4 Corrosion test

Corrosiveness of petroleum products indicates their tendency to cause metal corrosion. As copper is susceptible to corrosion, it is often used as an indicator of corrosiveness of petroleum products. The copper strip corrosion test is one of the most frequently used methods designed to assess the relative degree of corrosiveness of petroleum products. In the present study, the corrosiveness of neat HVI 350 lubricating oil and the oils formulated with 0.5%, 1.0 wt% and 1.5% of ODAP were evaluated on a copper strip corrosion tester following the Chinese standard test method GB/T 5096 procedures, which well conforms to ASTM D130. The test was performed by immersing a strip of cleaned, polished copper into 30 mL of a lubricating oil at 100 °C for 3 hours. Thereafter the color and tarnish of the strip surface was compared visually with copper corrosion standards and the degree of corrosiveness of the tested oil was assessed by rating the strip against the standards.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Effect of ODAP on biodegradability of lubricating oil

The effect of ODAP on biodegradability of HVI 350 lubricating oil after 8 days of biodegradation durations is shown in Fig. 2.

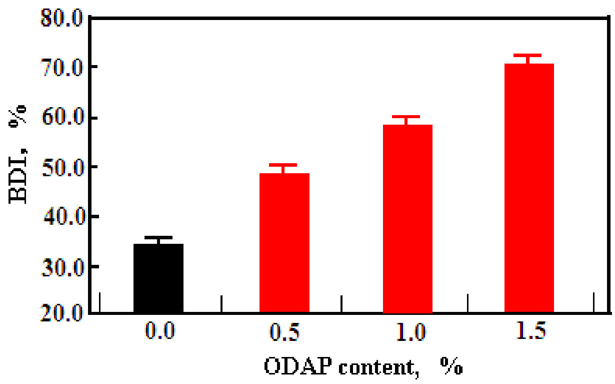


**Fig. 2.** Biodegradability of HVI 350 lubricating oil against contents of ODAP.

It can be observed clearly from Fig. 2 that incorporation of ODAP into HVI 350 mineral lubricating oil, at whatever contents, markedly enhanced biodegradability of the lubricating oil. The higher the ODAP content, the better the biodegradability of the oil. This indicated that ODAP acted as an effective biodegradation accelerant likely due to its effect as microbial nutrient, thus promoting microbe production. Increase of microbial populations in the biodegradation processes by incorporating phosphorous and nitrogenous biodegradation accelerants into an unreadily biodegradable mineral lubricating oil has been testified and reported previously by the authors [11,14].

As we know, biodegradability is not an exact property or characteristic of a substance, but is also a system's concept, i.e. a system with its conditions determines whether or not a substance within it is biodegraded. Studies have shown that many compounds such as phosphorous and nitrogenous ones, are highly effective in promoting hydrocarbons to biodegrade, and have been successfully employed in the bio-remediation of petroleum polluted areas such as water and soil [15-18]. Promotion of biodegradation of a mineral lubricating oil by ODAP is thus evidentially doable.

### 3.2 Effect of ODAP on anti-wear and friction-reducing capacities of lubricating oil

Shown in Figs. 3-5 are the maximum non-seizure loads ($P_B$), welding loads ($P_D$) and wear scar diameters (WSD) of HVI 350 mineral oil formulated with different contents of ODAP, respectively.

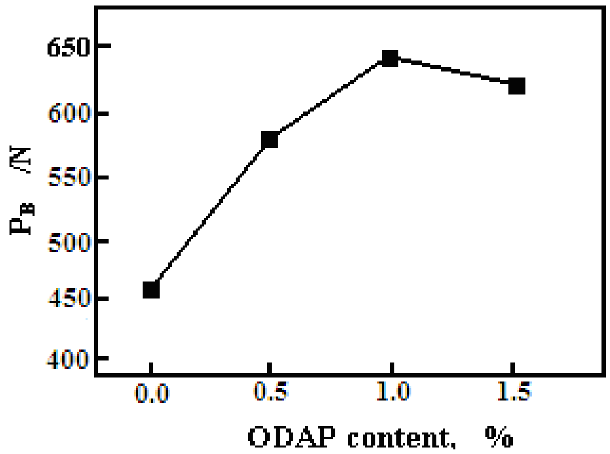


**Fig. 3.** Non-seizure loads versus ODAP contents.

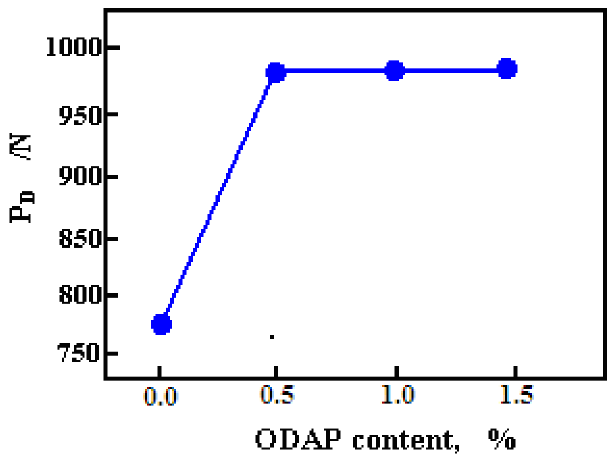


**Fig. 4.** Welding loads versus ODAP contents.

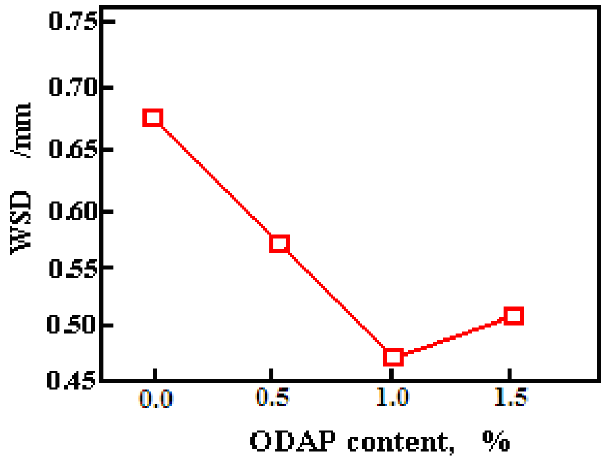


**Fig. 5.** Wear scar diameters versus ODAP contents.

It can be seen from Fig. 3 to Fig. 5 that, when formulated into HVI 350 mineral oil, ODAP to a great extent improved the anti-wear ability of the lubricating oil by exhibiting higher $P_B$, $P_D$ and lower WSD values than those of neat oil, although at ODAP content of 1.5%, the enhanced anti-wear ability of the oil slightly decreased.

Fig. 6 shows the friction coefficients of HVI 350 mineral oil and its formulations with different contents of ODAP versus test durations under the loads of 392N.

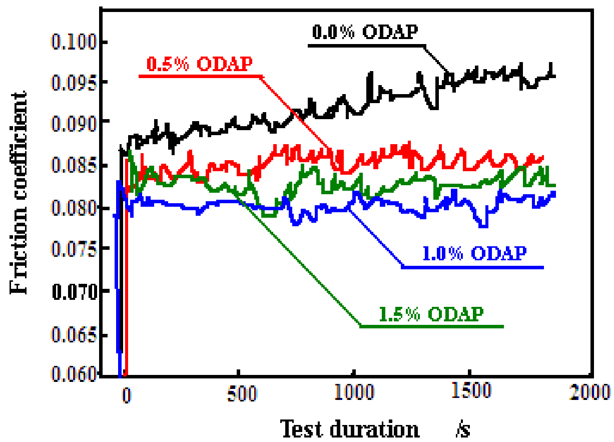


**Fig.6.** Friction coefficients versus test durations

From Fig. 6 we can see clearly that the friction coefficient of HVI 350 mineral oil was markedly reduced by ODAP. In the whole test durations of 1800 seconds, the oils containing ODAP of different contents all along provided lower friction coefficients than neat oil. The results indicated that ODAP was an effective friction-reducer for HVI 350 mineral oil.

### 3.3 Effect of ODAP on corrosiveness of lubricating oil

Shown in Table 1 are the corrosion test results of neat HVI 350 lubricating oil and the oils formulated with different contents of ODAP, respectively.

**Table 1.** Corrosion test results for neat oil and the formulated oils.

| Lubricating oil | Color of copper strip | Rating of copper strip |
|---|---|---|
| Neat oil | dark orange | 1b |
| Oil doped with 0.5% of ODAP | Light orange, almost the same as a new polished strip. | 1a |
| Oil doped with 1.0% of ODAP | Light orange, almost the same as a new polished strip. | 1a |
| Oil doped with 1.5% of ODAP | Light orange, almost the same as a new polished strip. | 1a |

It can be seen from Table 1 that the excellent ratings of copper strips of “1b” for neat HVI 350 lubricating oil and “1a” for all the oils formulated with ODAP demonstrated that the corrosiveness of neat oil and the formulated oils was indeed negligible. The neat oil and the formulated oils can be regarded as being non-corrosive. This indicated that the impact of ODAP on corrosiveness of the lubricating oil were not obvious, although the formulated oils seemed to provide slightly better corrosion inhibiting ability.

## 4. CONCLUSIONS

Oleic acid diethanolamide phosphate, when incorporated into a non-biodegradable mineral lubricating oil such as HVI 350 oil, markedly promoted biodegradation of the lubricating oil by exhibiting higher biodegradability. It also to a great extent fortified the anti-wear and friction-reducing capacities of the oil by providing higher $P_B$, $P_D$ and lower WSD. On the other hand, impact of ODAP on corrosiveness of the lubricating oil was unobvious. The corrosion inhibiting abilities of neat oil and the ODAP-doped oils were excellent.

## Acknowledgement

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## REFERENCES

[1] F. Haus, G. Jean, G.A. Junter: *Primary biodegradability of mineral base oils in relation to their chemical and physical characteristics*, Chemosphere, Vol. 45, No. 6, pp. 983-990, 2001.

[2] W.J. Bartz: *Lubricants and the environment*, Tribology International, Vol. 31, No. 1-3, pp. 35-47, 1998.

[3] S.Z. Erhan, S. Asadauskas: *Lubricant basestocks from vegetable oils*, Industrial Crops and Products, Vol. 11, No. 2, pp. 277-282, 2000.

[4] S. Boyde: *Green lubricants: environmental benefits and impacts on lubrication*, Green Chemistry, Vol. 12, No. 4, pp. 293-307, 2002.

[5] A. Willing: *Lubricants based on renewable resources - an environmentally compatible alternative to mineral oil products,* Chemosphere, No. 43, pp. 89-98, 2001.

[6] G. Rebeccal, M. Rogere: *Biodegradable lubricants,* Lubrication Engineering, Vol. 54, No. 7, pp. 10-17, 1998.

[7] N.J. Fox, G.W. Stachowiak: *Vegetable oil-based lubricants - a review of oxidation,* Tribology International, Vol. 40, No. 7, pp. 1035–1046, 2007.

[8] S.J. Randles, M. Wright: *Environmentally considerate ester lubricants for automotive and engineering industries,* Journal of the Synthetic Lubrication, Vol. 9, No. 2, pp. 145–161, 1992.

[9] K. Cheenkachorn, B. Fungtammasan: *Development of engine oil using palm oil as a base stock for four-stroke engines*, Energy, Vol. 35, No. 6, pp. 2552-2556, 2010.

[10] S.H. Roby, J.A. Supp: *Formulating for ILSAC GF-2—Part 1: obtaining valve train wear protection while reducing the phosphorus content of a motor oil,* Society of Automotive Engineers [Special Publication], Vol. 1121, pp. 23-27, 1995.

[11] B.S. Chen, J.H. Fang: *Enhancement of biodegradability of lubricants by biodegradation accelerants*, Lubrication Science, Vol. 20, No. 4, pp. 311-317, 2008.

[12] K. Liang, B.S. Chen, N. Zhang, J.H. Fang: *Effect of Oleic Diethanolamide Phosphate on Biodegradability and Lubricity of Lubricating Oil,*

Petroleum Processing and Petrochemicals, Vol. 43, No. 1, pp. 68-71, 2012.

[13] K. Wang, J.H. Fang, B.S. Chen: *A fast method for evaluating biodegradability of lubricants*, Acta Ptrolei Sinica (Petroleum processing Section), Vol. 23, No. 6, pp. 74-78, 2004.

[14] B.S. Chen, N. Zhang: *Impact of fatty acyl amino acids on biodegradation of mineral oil,* Chinese Journal of Environmental Engineering, Vol. 3, No. 6, pp. 1140-1142, 2009.

[15] T. Sobisch, H. Niebelschutz: *Effect of additives on biodegradation of PAH in soils,* Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 162, No. 1-3, pp. 1-14, 2000.

[16] M. Molnar, L. Leitgib: *Enhanced biodegradation of transformer oil in soils with cyclodextrin – from the laboratory to the field,* Biodegradation, Vol. 16, No. 2, pp. 159-168, 2005.

[17] X.Y. Li, D.Z. Wei: *Effect of nitrogenous and phosphorous compounds on degradation of microbes,* Nonferrous Metals, Vol. 21, No. 4, pp. 237-239, 2000.

[18] K.S.M. Rahman, T.J. Rahman: *Enhanced bioremediation of n-alkane in petroleum sludge using bacterial consortium amended with rhamnolipid and micronutrients,* Bioresource Technology, Vol. 90, No. 2, pp. 159-168, 2003.