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ANTIOXIDANTS AND CHARGE CONTROL ADDITIVES FOR ESTER OILS

Non-Ferrous

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INTRODUCTION

Fluid dynamic bearing spindle motors are now ubiquitous in magnetic recording disk drives. Areas of continuous improvement for these motor bearings are minimizing the motor voltage and electric charge buildup in the oil and limiting oil oxidation. This talk describes the development of an ester oil formulation with antistatic additives and a kinetic model for synergistic formulation of antioxidants. Novel polyaromatic charge control additives have the potential to offer improved motor voltage stability relative to the currently used aromatic amines. A kinetic model that includes the synergistic effects of primary and secondary antioxidants and metal catalyst on oil oxidation lifetime is employed to guide the formulation. Knowledge of the chemistry provides a significant benefit because it reduces the development cycle time and lowers the total cost to obtain improved motor lifetime.

OXIDATION AND STABILIZATION CHEMISTRY MODEL

The complete model is presented in [1] and numerical simulation with relative rate constants is shown in [2]. A condensed version of the model is given here in Fig. 1. The base oil is represented as "oil" in the schematic. Initially, a carbon radical forms thermally or mechano-chemically on the oil molecule in a sliding interface. The carbon radical combines with oxygen to form a peroxy radical. Two reaction pathways are possible for the peroxy radical. The peroxy radical can abstract a proton from an adjacent oil molecule (interchain). Interchain proton abstraction forms a new carbon radical and a hydroperoxide. The hydroperoxide slowly decomposes into an alkoxy radical and a hydroxy radical. The hydroxy radical abstracts a chain proton from the oil, which forms a new carbon radical and water. The alkoxy radical abstracts a proton from the oil, which forms a new carbon radical and leaves a hydroxyl group on the original oil chain. Hydroxyl groups increase the oil viscosity through hydrogen bonding. Returning to the other reaction pathway available to the peroxy radical -- The peroxy radical can abstract an adjacent proton from the same oil molecule (intrachain). This produces a new carbon radical and leads to more products including chain cleavage [3]. Chain cleavage forms shorter chains with methyl ketone or acid end groups.

Acidic oxidation products dissolve trace amounts of catalytic metals into the oil. Iron, chromium, and copper catalyze the decomposition and formation of hydroperoxide, according to the reduction-oxidation shuttle mechanism [4,5], which greatly increases the oxidation rate.

Oxidation is inhibited by antioxidant. Primary antioxidant protonates the radicals [6], and secondary antioxidant decomposes peroxides [7], thus interrupting the mechanism shown in Fig. 1. Even though most of the radicals are quenched by the antioxidant, a small but finite amount of oxidation continues. The oxidation products include carboxylic acids. Carboxylic acids dissolve catalytic metal ions into the oil. A small amount of catalytic metal is still dissolved when antioxidants alone are used. Metal passivator, such as tricresyl phosphate TCP [8] or corrosion inhibitors [9] along with the antioxidants moderates the metal dissolution. The combination of primary and secondary antioxidant, and metal passivator or corrosion inhibitor, provide a "synergistic" stabilization of the oil in the presence of catalytic metal bearing surfaces.

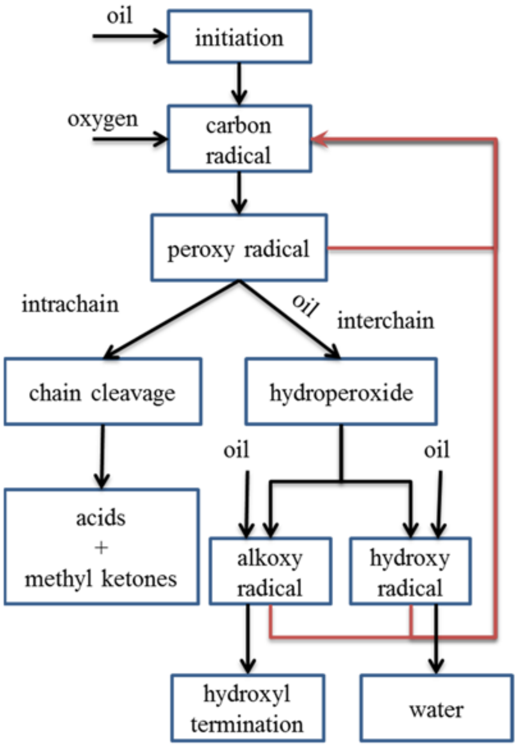


Figure 1. Schematic representation of the base oil oxidation mechanism.

Polyaromatic antioxidants were also found to function as charge control agents [10]. However, since antioxidants are depleted over time, both the loss of functionality and the contribution of degradation products changes the oil electrical properties. Chemically stable polyaromatic compounds which act as charge transfer agents were grafted onto the core of the ester base oil to solubilize them in the formulation and to stabilize the electrical properties.

RESULTS AND DISCUSSION

A pentarythritol tetraester oil was formulated with different proportions of primary antioxidant dioctyldiphenylamine (DDA) and secondary antioxidant zinc dialkyldithiocarbamate (ZDTC) with and without 1 wt% of TCP. The DDA + ZDTC concentration was maintained at 1 wt%. These oils were heated in a loosely covered beaker with ball bearings in an oven at 170 °C until the onset of sudden degradation [1,2]. The oil lifetime is shown as a function of the molar ratio in Fig. 2. The longest lifetime was between 0.1 and 0.2 with no TCP. In the absence of wear, the acidic TCP may degrade the oil lifetime by metal dissolution.

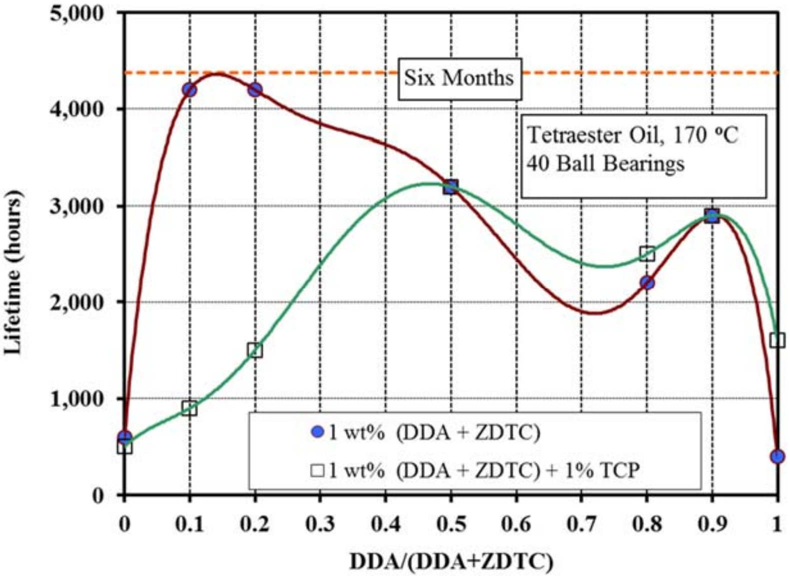


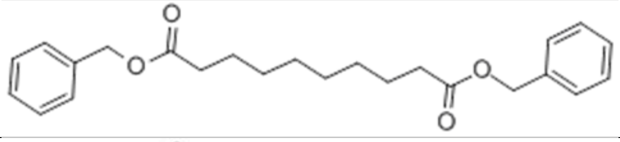
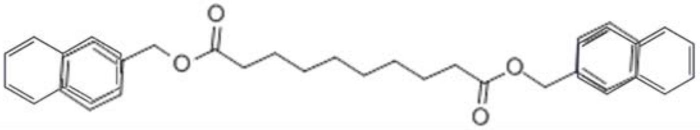
Figure 2. Oil oxidation lifetime as a function of the molar ratio of primary to primary + secondary antioxidant measured at 170 °C in pentaerythritol tetraester oil containing ball bearings with total antioxidant amount 1 wt%

The effect of catalytic metals and corrosion inhibitor on oil lifetime were measured. The base oil was di(2-ethyl hexyl) sebacate. Bronze powder significantly decreased the oil lifetime due to dissolution of catalytic copper into the oil, even though the oil contained a good primary antioxidant. Corrosion inhibitors were tested to help prevent metal dissolution. The most effective corrosion inhibitor was tolutriazole (5-Methyl-1H-benzotriazole). Even though 1% 1H-benzotriazole provided a slightly longer lifetime, it was evaporating from the oil and crystallizing on the flask.

There is also a significant effect of base oil molecular structure on the oil lifetime. A pentaerythritol tetraester had almost 2x the lifetime of diester oils. In view of the oxidation mechanism, Fig. 1, the molecular structure probably influences the rate of intrachain vs. interchain pathway. The structure with the longer lifetime favors the interchain pathway which leads to inert hydroxyl and water rather than the intrachain pathway which forms acid.

Two examples of the novel charge transfer agents esterified onto the sebacic acid core of the di(2-ethylhexyl)sebacate are shown on Table 1 [11]. The symmetric aryl esters, with the same group attached to both ends of the diacid, dibenzyl sebacate, diphenethyl sebacate, and dinaphthyl sebacate are solid at room temperature, and are useful as soluble charge control additives. The asymmetric aryl esters (benzyl, 2-ethylhexyl) sebacate, (phenethyl, 2-ethylhexyl) sebacate, and (phenethyl, 2-ethylhexyl) adipate are liquids at room temperature. The asymmetric aryl esters may be useful as a conductive fluid lubricant without the necessity to dissolve them in a base oil. All of the aryl esters were completely soluble in the base oil di(2-ethylhexyl) sebacate at least up to 5 wt%.

Table 1. Two diaryl esters based on the sebacic acid core.

dibenzyl sebacate	
dinaphthyl sebacate	

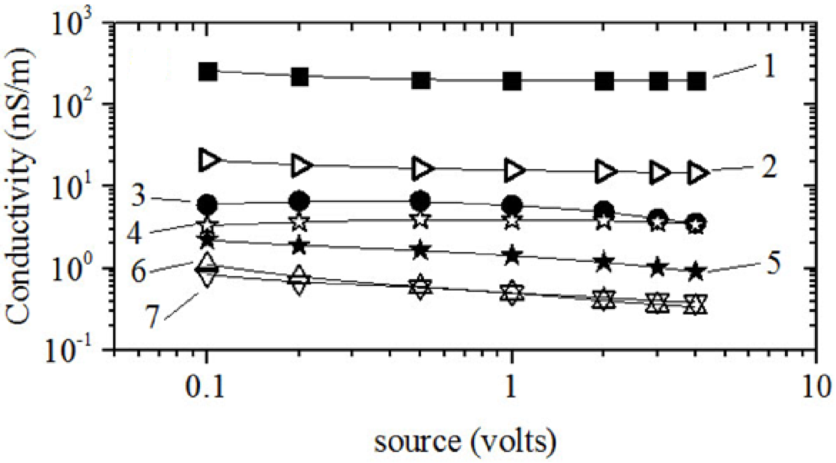


Figure 3. Conductivity vs. source voltage 1 - 0.5% STADIS 450 in NPG, 2 - (benzyl, 2-ethylhexyl) sebacate, 3 - 2% Vanlube 9317 in NPG, 4 - 5% dinaphthyl sebacate in DOS, 5 - 1% dinaphthyl sebacate in DOS, 6 - NPG base oil, 7 - DOS base oil. Measured at ambient temperature 25 °C.

Figure 3 shows the conductivity vs. source voltage for several of the aryl modified charge control oils compared with the pure base oil and two types of oils that were tested in fluid bearing motor for disk drives, DOS oil in Table 17 and NPG oil neopentyl glycol dicaprate (decanoic acid,1,1'-(2,2-dimethyl-1,3-propanediyl) ester, CAS 27841-06-1). The 0.5% STADIS 450 (Octel Starreon L.L.C., 8375 S. Willow St., Littleton, CO 80124) in NPG base oil was highly conductive but the accumulated charge was too high. The conductivity of the pure base oil is so low that a high voltage is built up across the bearing, which degrades the reliability of the head disk interface. The combination of 2% Vanlube 9317 (50 wt% reaction mixture of dioctyl diphenyl amine and phenyl naphthyl amine in a tetraester oil carrier, R.T. Vanderbilt Corp.) [12] in NPG is known to provide both sufficient conductivity and acceptably low permeability for fluid bearing motors in magnetic recording disk drives. However, Vanlube 9317 is an antioxidant, hence is an unstable species to rely on for long term stability of charge control and interface reliability.

The most promising chemically stable aryl charge control agent is the dinaphthyl sebacate, which is shown at 1 and 5 wt% in DOS in Fig. 3. The electrical properties of the 5 wt% formulation are sufficiently close to those of the 2% Vanlube 9317 in NPG. Therefore the 5 wt% dinaphthyl sebacate can provide a more stable voltage and reliable magnetic recording interface. Also shown in Fig. 3 is the (benzyl, 2-ethylhexyl) sebacate. This asymmetric aryl/alkyl ester may be useful alone as a formulated base oil where a highly conductive bearing oil or grease is desirable in disk drives, other electromechanical devices, or to limit flow electrification in synthetic oil for electrical transformers [13].

REFERENCES

[1] Karis, T.E., 2003, "Lubricant Additives for Magnetic Recording Disk Drives," in: Lubricant Additives: Chemistry and Applications, L. Rudnick (ed.), pp. 467-511, Marcel Dekker, New York.
[2] Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology, 2^nd edition*, Chapter 40, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2013.
[3] Karis, T.E., Miller, J.L., Hunziker, H.E., de Vries, M.S., Hopper, D.A., and Nagaraj, H.S., 1999, "Oxidation Chemistry of a Pentaerythritol Tetraester Oil," *Trib. Trans.*, **42**(3), pp. 431-442
[4] Bondi, A., 1951, Physical Chemistry of Lubricating Oils, Reinhold Publishing Corporation, New York, pp. 292-332.
[5] Chakravarty, N.K., 1963, "The Influence of Lead, Iron, Tin, and Copper on the Oxidation of Lubricating Oils. Part II. On the Metal Catalysed Oxidation of Oils," *J. Inst. Petrol.*, **49**(479), pp. 353-358.
[6] Ischuk, Y.L., and Butovets, V.V., 1991, "Estimation of Grease Oxidation Stability Under Dynamic Conditions and Antioxidant Testing," *NGLI Spokesman*, **55**(4), pp. 133-138.
[7] Shelkova, R.G., Kuz'mina, G. N., Sanin, P. I., and Parenago, O. P., 1991, "Kinetics of the High-Temperature Oxidation of Hydrocarbons Inhibited by Metal Dialkyldithiocarbamates," *Kinet Catal*, **31**(5), Part 2, pp. 1094-1098.
[8] Lockwood, F., and Klaus, E.E., 1982, "Ester Oxidation- The Effects of an Iron Surface," *ASLE Transactions*, **25**(2), pp. 236-244.
[9] Burns, J.M., Carter, M.D., Karis, T.E., Shida, K, .and Wong, S.Y., 2009 "Fluid Dynamic Bearing Comprising a Lubricating Fluid Having Tolutriazole," *US patent* 7,535,673.
[10] T.E. Karis, "Surfactants for Electric Charge and Evaporation Control in Fluid Bearing Motor Oil," pp. 437-462, in Surfactants in Tribology Volume 3, G. Biresaw and K. L. Mittal, Editors, CRC Press, Taylor & Francis Group, LLC, Boca Raton, FL, (2013).
[11] T. Karis, "Charge control agent for fluid dynamic bearing motor lubricant," US 2016/0086631 A1.
[12] P. Bartle and Chr. Volkl, "Thermo-oxidative stability of high-temperature stability polyol ester jet engine oils — a comparison of test methods," J. Synth. Lubrication, 17, 179-189 (2000).
[13] T. Toudja, F. Chetibi, A. Beldjilali, H. Moulai, and A. Beroual, "Electrical and physicochemical properties of mineral and vegetable oils mixtures," Dielectric Liquids (ICDL), 2014 IEEE 18th International Conference on, Page(s):1- 4.