Controlling Mechanochemical Tribofilm Growth

James P. Ewen,[1)]* Jie Zhang, [1)] and Hugh A. Spikes[1)]
[1)] Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK
*Corresponding author: j.ewen@imperial.ac.uk

Mechanochemistry is known to play a key role in the function of some lubricant additives, such as the tribofilm growth of zinc dialkyldithiophosphate (ZDDP). We study the tribofilm formation rate of ZDDPs containing several different alkyl groups on steel surfaces from a high-friction base oil. We use macroscale tribometer experiments under full-film elastohydrodynamic lubrication conditions to enable careful control of the temperature and stress during tribofilm growth. We show how the chain length and the presence of branches or bulky cycloaliphatic groups can lead to large differences in the temperature- and stress-dependencies of the tribofilm formation rate, which can be explained through variations in packing density, steric hindrance, and stress transmission efficiency. Our rate data are successfully fitted using the Bell model; a simple modification of the Arrhenius equation that is commonly employed to model the kinetics of mechanochemical processes. Using this model, we observe large differences in the activation energy, pre-exponential factor, and activation volume for the various ZDDPs. Our findings show how structure–performance relationships can be identified for lubricant additives, which may be useful to optimise their molecular structure.

Keywords (from 3 to 5 max): mechanochemistry, zinc dialkyldithiophosphate, tribofilms

1. Introduction

ZDDP reduces wear by forming protective 'tribofilms' on rubbing steel surfaces. Despite decades of research and development to find a more environmentally-friendly alternative, ZDDP remains ubiquitous in engine lubricants. To rationally design antiwear additives with improved performance, a molecular-level understanding of the tribofilm formation and wear-reduction mechanisms of ZDDP is first required. The tribofilms formed by ZDDP on steel substrates are mainly composed of zinc and iron polyphosphates. These are formed by nucleophilic substitution reactions at the P atoms, which result in the formation of the P–O–P chains. These reactions are dramatically accelerated once some of the alkyl or aryl groups (that are required to ensure the solubility of ZDDP in the base oil) are removed. Therefore, ZDDPs containing different alkyl and aryl groups show greatly varying tribofilm growth and antiwear performance; however, the underlying molecular mechanisms for these differences in macroscale behavior remain unclear.

2. Methods

We performed ball-on-disk tribometer experiments using steel/steel contacts with the Extreme-pressure Traction Machine (ETM) from PCS Instruments. The tribofilm thickness was periodically monitored using Spacer-layer Imaging (SLIM). The ZDDPs were synthesized from the corresponding high-purity alcohols by Afton Chemical. Four primary (oct-1-yl, 2-ethylhexyl, 2-cyclohexylethyl, and dodec-1-yl) and three secondary (oct-2-yl, but-2-yl, and 4-methylpent-2-yl) ZDDPs were synthesised. Indopol H-8, a high-friction polybutene oligomer from INEOS was used as the base fluid.

3. Results and Discussion

Figure 1 shows how the tribofilm thickness varies with rubbing time for two ZDDP solutions in Indopol-H8 at the same concentration (800 ppm P), temperature (80 °C) and load (1000 N) condition. The secondary oct-2-yl ZDDP has a much higher tribofilm growth rate than the primary oct-1-yl ZDDP.

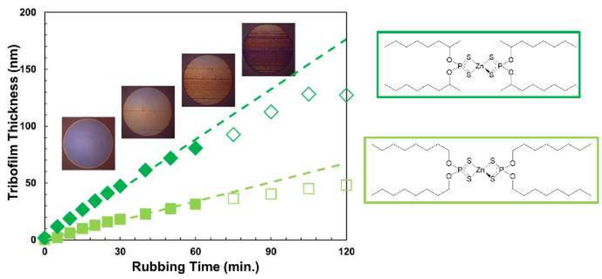

Figure 1: Comparison of the tribofilm growth of secondary (oct-2-yl) and primary (oct-1-yl) ZDDPs.

We find that the seven different ZDDPs have very different tribofilm formation rates. For all the ZDDPs, the tribofilm growth rate increases exponentially with temperature and shear stress, which confirms that this is a stress-augmented, thermally-activated process. We observe large differences in the temperature- and shear stress-dependencies of the various ZDDPs. We have shown how the parameters for the Bell equation can be used to rationalise the order of mechanochemical reactivity for the different ZDDPs. Our results suggest that the chain length, branching and presence of bulky cycloaliphatic groups in the ZDDP alkyl substituents may affect the packing density, steric hindrance, and stress transmission, and result in significant differences in the activation energy, pre-exponential factor, and activation volume.

4. References

[1] Zhang, J; Ewen, J.P., Spikes, H.A. "Substituent effects on the mechanochemical response of zinc dialkyldithiophosphate" Mol. Syst. Des. Eng. 2022. DOI: https://doi.org/10.1039/D2ME00049K

[2] Zhang, J, et al. "Mechanochemistry of Zinc Dialkyldithiophosphate on Steel Surfaces under Elastohydrodynamic Lubrication Conditions" ACS Appl. Mater. Interfaces 12, 6662-6676, 2020.