

Nanoscale *in situ* Studies of Anti-Wear Tribochemical Film Formation

Robert W. Carpick ^{1)*}

¹⁾ University of Pennsylvania, Philadelphia, PA, USA

*Corresponding author: carpick@seas.upenn.edu

New insights into anti-wear (AW) tribofilm formation are derived using *in situ* methods based on atomic force microscopy (AFM). First, for zinc dialkyldithiophosphates (ZDDPs), we previously reported an AFM-based approach for visualizing the tribochemical formation of ZDDP AW films *in situ* at the nanoscale on iron. New results show how tribofilm growth occurs on other substrates, provided they have sufficient mechanical hardness. We also study *in situ* growth of AW tribofilms formed with zirconia nanoparticles dispersed in oils.

Keywords: ZDDP, zirconia nanoparticle, anti-wear tribofilm, *in situ* AFM, nanotribology

1. Introduction

Modern lubricants are composed of base oils with an array of crucial additives with multiple functionalities. Of these, anti-wear (AW) additives are of particular interest. One of the most crucial modern AW additives is zinc dialkyldithiophosphate (ZDDP)¹. Achieving a deeper understanding of how ZDDP forms protective tribofilms is motivated by the desire to reduce Zn-, P- and S-containing compounds in the exhaust, which reduce the catalytic converter's efficiency and lifetime. More broadly, increasing the mechanical efficiency of any lubricated system by reducing lubricant viscosity leads to increased boundary contact, necessitating AW additives that can withstand the resulting harsh conditions. Here we use atomic force microscopy (AFM) to develop new insights at the nanoscale into tribofilm formation mechanisms for ZDDP-containing lubricants, and for lubricants containing a novel zirconia AW additive.

2. Methods

Single-asperity studies are conducted here with AFM, where the nanometer-scale AFM tip is slid against a substrate of desired composition, while immersed in additive-containing base stock, usually a polyalphaolefin (PAO) oil (Fig. 1). This can be done with nanoscale² or microscale³ probes.

3. Results and Discussion

We previously developed a novel AFM-based approach for visualizing and quantifying the tribochemical formation of ZDDP AW films *in situ* at the nanoscale. We observed that film growth follows an stress-assisted Arrhenius model of growth, which explains the films' graded structure and their self-limiting behavior². New results show how tribofilm growth occurs independent of the substrate, provided it has sufficient mechanical hardness. In the case of aluminum, insufficient hardness leads to plastic deformation of the substrate; the resultant strain-hardened material eventually develops sufficient hardness to support tribofilm growth⁴.

We also observe growth of anti-wear tribofilms formed in a dispersion of zirconia nanoparticles in oil *in situ*⁵. The commercial viability and efficacy as a drop-in additive of this nanoparticle depends significantly on nanoparticle interactions with other additives, such as

ZDDP. We show that the films form readily even in a fully-formulated commercial-grade gear-oil⁶. These tribofilm growth mechanisms also permit using AFM to pattern surfaces with nanoscale features⁷.

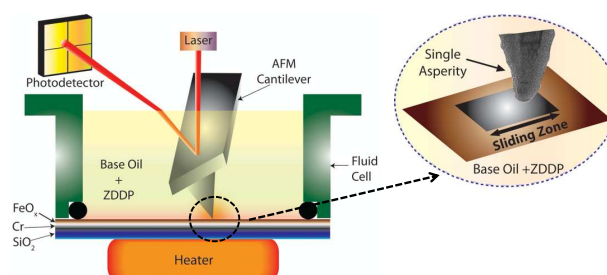


Fig. 1: Schematic of setup used for tribofilm formation.

4. References

- [1] Spikes, H.A. "The History and Mechanisms of ZDDP," *Tribol. Lett.*, 17, 2004, 469.
- [2] Gosvami, N.N., Bares, J.A., Mangolini, F., Konicek, A.R., Yablon, D.G. and Carpick, R.W. "Mechanisms of Antiwear Tribofilm Growth Revealed in Situ by Single-Asperity Sliding Contacts," *Science*, 348, 2015, 102.
- [3] Gosvami, N.N., Ma, J. and Carpick, R.W. "An in Situ Method for Simultaneous Friction Measurements and Imaging of Interfacial Tribochemical Film Growth in Lubricated Contacts," *Tribol. Lett.*, 66, 2018, 154.
- [4] Gosvami, N.N., Lahouij, I., Ma, J. and Carpick, R.W. "Nanoscale in Situ Study of ZDDP Tribofilm Growth at Aluminum-Based Interfaces Using Atomic Force Microscopy," *Trib. Int.*, 143, 2020, 106075.
- [5] Khare, H.S., Lahouij, I., Jackson, A., Feng, G., Chen, Z., Cooper, G.D. and Carpick, R.W. "Nanoscale Generation of Robust Solid Films from Liquid-Dispersed Nanoparticles Via in Situ Atomic Force Microscopy: Growth Kinetics and Nanomechanical Properties," *ACS Appl. Mat. Interf.*, 10, 2018, 40335.
- [6] Elinski, M.B., LaMascus, P., Zheng, L., Jackson, A., Wiacek, R.J. and Carpick, R.W. "Cooperativity between Zirconium Dioxide Nanoparticles and Extreme Pressure Additives in Forming Protective Tribofilms: Toward Enabling Low Viscosity Lubricants," *Tribol. Lett.*, 68, 2020, 107.
- [7] Khare, H.S., Gosvami, N.N., Lahouij, I., Milne, Z.B., McClim, J.B. and Carpick, R.W. "Nanotribological Printing: A Nanoscale Additive Manufacturing Method," *Nano Lett.*, 18, 2018, 6756.