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

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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 nanoscale[2] or microscale[3] 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 behavior[2]. 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 growth[4].

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-oil[6]. These tribofilm growth mechanisms also permit using AFM to pattern surfaces with nanoscale features[7].

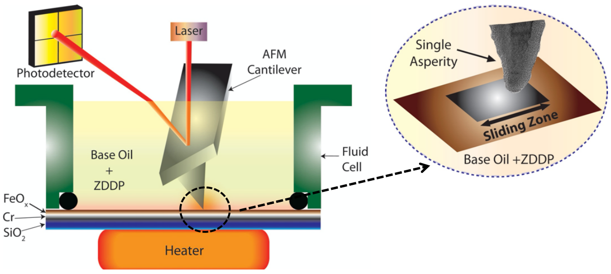

Fig. 1: Schematic of setup used for tribofilm formation.

4. References

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