In-situ study of growth mechanisms and kinetics of ZDDP anti-wear tribofilms in nanoscale single-asperity contacts

N. N. Gosvami[1], J. A. Bares[1,5], F. Mangolini[2], A. R. Konicek[3], Alan M. Schilowitz[3], D. G. Yablon[4,3], and R. W. Carpick[1]

[1] Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA.
[2] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
[3] Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, USA
[4] SurfaceChar LLC, Sharon, MA 02067, USA
[5] Present address: BorgWarner Powertrain Technical Center, Auburn Hills, MI 48326, USA

Zinc dialkyldithiophosphates (ZDDPs) are lubricant additives used nearly universally in engine oils. Despite the generation of volatile phosphorous- and sulphur-containing compounds in the downstream gases that can reduce the working life of the catalytic converter, the unrivaled wear protection of ZDDPs makes them essential to the lubricant performance. ZDDPs work by decomposing under tribological sliding to form nanoscale anti-wear films whose growth mechanisms are still poorly understood due to the complexity of the macroscopic multi-asperity sliding interfaces and the multiple chemical species involved. Greater understanding of the formation of these films is essential to enable rational design of more environmentally-friendly and energy-efficient engine oil formulations. Here we report a novel experimental approach using atomic force microscopy (AFM) for visualizing and quantifying the formation of ZDDP anti-wear films in-situ in a single asperity contact with nanometer-scale spatial resolution. Experiments performed on iron-coated silicon surfaces at 80-140 ^{o}C in the presence of ZDDP containing polyalphaolefin oil show that thermal films grow on the substrate in the absence of tribological contact. These films are easily removed by sliding the tip at applied normal forces of only a few nanonewtons (contact pressure < 1.0 GPa). Continued sliding at higher normal loads (contact pressure ~ 2.0 -6.0 GPa) reveals the nucleation and growth of much more robust films with a pad-like lateral structure, similar to their morphology in macroscopic contacts. The growth rate is nonlinear with time, and increases exponentially with temperature and contact pressure, in agreement with the reaction rate theory. This is the first direct confirmation and quantification of asperity-level formation of ZDDP-derived anti-wear films, enabling us to directly compare with atomistic predictions and other possible proposed mechanisms.