

# **The Surface Chemistry of Boundary Film Formation**

**Wilfred T. Tysoe**

Department of Chemistry and Laboratory for Surface Studies, University of  
Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

**E-mail: [wtt@uwm.edu](mailto:wtt@uwm.edu)**

Additives are added to lubricants, which react with the surfaces to form a boundary lubricating film that can lower friction and/or prevent wear. In order to understand the chemistry of the film-formation processes, the sliding interface should be at thermodynamic equilibrium. It is argued that this occurs at the high interfacial temperatures that occur under so-called extreme-pressure (EP) conditions, where interfacial temperatures  $\sim 1000$  K. Here, the surface reaction and film growth kinetics are dominated by thermal processes and this chemistry is illustrated using simple chlorinated hydrocarbons as model additives. At the other extreme, the interface is at thermodynamic equilibrium under very mild conditions, where the surface temperature rise is low. In this case, films can be formed by a shear-induced, surface-to-bulk transport mechanism. This effect is investigated by studying model sulfur- and boron-containing additives on copper. Experiments are carried out in ultrahigh vacuum (UHV) to understand the surface chemistry. The nature of the surface species that are formed by reaction with the model lubricant additive is investigated using a range of surface analytical techniques such as temperature-programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). The effect of rubbing these adsorbate-covered surfaces is investigated, also in UHV, by measuring the friction coefficient and contact resistance during rubbing. The chemical composition of the resulting boundary films are also analyzed to provide a full understanding of the tribochemical reactions.

**Keywords:** tribochemistry; boundary films; lubricant additives