

Café Scientifique invité

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THERMAL AND SHEAR-INDUCED EFFECTS IN BOUNDARY FILM FORMATION

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The formation of a boundary film by reaction with a gas-phase lubricant or lubricant additive formally occurs in several steps that involve the initial adsorption and reaction of the lubricant molecule on the surface, followed by shear-induced decomposition and formation of the boundary film. Fully understanding this sequence of reaction steps will enable the structure of the additive molecule to be related to the nature of the resulting boundary lubricating film. Systems are studied for which the interface is at thermodynamic equilibrium to allow kinetic models, such as transition-state theory to be applied.

The first regime for which the system is in thermodynamics equilibrium is when the interfacial temperatures are high (~1000 K), so-called extreme-pressure (EP) lubrication. Here, the film formation pathways are dominated by thermal reactions at the surface. This chemistry is illustrated using the example of small chlorinated hydrocarbons reacting with iron surfaces.

The second regime occurs under mild sliding conditions for which the interfacial temperature rise is small. The tribochemistry in this regime investigated by carrying out friction measurements using an ultrahigh vacuum tribometer, by analyzing the elemental composition in the wear track region using Auger spectroscopy and by detecting gas-phase products evolved during sliding.

The approach is illustrated using several examples. First is gas-phase lubrication of copper by dialkyl disulfides and trisulfides. They initially react to form thiolate species on the surface and shear at the interface causes sulfur and some carbon to penetrate the substrate to form a boundary film that reduces friction. The variation in the amount of methane desorbing from the surface per pass during sliding allows the shear-induced rate of thiolate reaction to be measured, allowing models for the shear-induced decomposition to be tested experimentally.

In a second example, the tribological chemistry of borate esters on copper is explored using isopropoxy tetramethyl dioxaborolane (ITDB), and tetramethyl dioxaborolane (TDB) as gas-phase lubricants. TDB decomposes to deposit BO_x species on the surface and produces an initial decrease in friction coefficient that is not sustained. ITDB, which reacts at room temperature to form a surface tetramethyl dioxaborolide species, results in an immediate and sustained decrease in friction coefficient when used as a gas-phase lubricant for copper. Thus, the surface chemistry of the borate esters can be correlated with their tribological properties and illustrates that replacing a hydrogen atom in TDB with a 2-propoxy group in ITDB has a profound influence on both the surface and tribological chemistry.