UNDERSTANDING THE TRIBOLOGICAL CHEMISTRY OF CHLORINE- AND SULFUR- AND PHOSPHORUS-CONTAINING ADDITIVES

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ABSTRACT
Chlorine- and sulfur- and phosphorus-containing compounds are commonly added to the base fluid to synthesize lubricants used under extreme-pressure (EP) conditions. Analyzing the resulting tribological films on iron reveals that chlorinated hydrocarbons thermally decompose forming a layer that consists of iron chloride (FeCl₂) or carbide (Fe₃C), and that dialkyldisulfides react to form FeS and Fe₃C. Alkyl phosphates thermally decompose on iron oxide to form alkyl and alkoxy, as well as POₓ species, on the surface. The alkyl and alkoxy species thermally decompose on heating to evolve gas-phase products and deposit carbon onto the surface. The POₓ species rapidly diffuse into the oxide forming a film that consists of a carbonaceous layer covering a phosphate film. The tribological properties of evaporated and reactively grown thin films have been investigated in ultrahigh vacuum. This strategy eliminates contamination and allows films of known composition and structure to be grown on well-characterized substrates. Three tribological regimes are identified depending on film thickness. In the first regime, an initial rapid decrease in friction is found when a film that is a few nanometers thick (corresponding to a monolayer) covers the surface. The friction coefficient increases once again in the second regime as the film becomes thicker, due to the increased contact area between the film and the rough tribotip, and the behavior is well described by a modified Greenwood-Williamson model. A third regime is found when the film becomes thicker than the interfacial roughness, where the surfaces are completely separated by the film. Finally, measuring the friction coefficients of thin halide films deposited onto various substrates, where the local pressure at the asperity tips depends on the substrate hardness, shows that the shear strength of the “monolayer” films depends on pressure.

Keywords: tribological films, ultrahigh vacuum tribometer, friction.

INTRODUCTION
It has been shown previously that chlorinated hydrocarbons thermally decompose on an iron surface during extreme-pressure lubrication to form a film that consists of FeCl₂, which incorporates small carbonaceous particles [1-14]. In addition, particularly when carbon tetrachloride is used as an additive, carbon diffuses into the bulk of the iron sample to form a carbide [15]. It has further been shown that this chemistry can be reproduced in ultrahigh vacuum using molecular beams of chlorinated hydrocarbons incident onto a heated iron sample [15-18]. In this case, the nature of the gas-phase reaction products can be determined using a mass spectrometer. It was found that the variation in the rate of product formation as a function of sample temperature yielded an activation energy that was in good agreement with similar values from the temperature dependence of the film growth rate measured at higher pressures in a microbalance. Since the reactively formed tribological interfaces are relatively complicated, we have embarked on a study of thin inorganic films on iron measured using an ultrahigh vacuum tribometer. These studies were initiated using potassium chloride since it has a relatively low shear strength [19]. They showed that the high friction coefficient of the initially clean surface (~2) was reduced to 0.27 ± 0.03 by the addition of ~40 Å of KCl. It was also found that the completion of the first KCl monolayer was responsible for the reduction in friction [20]. The deposition of thicker films leads to an increase in friction due to an increase in contact area between the film and rough tribopin [21]. Finally, preliminary quantum mechanical calculations are carried out to explore the shear behavior of thin KCl films on iron.

EXPERIMENTAL
Experiments were carried out in a stainless steel, ultrahigh vacuum chambers operating at base pressures of 5×10⁻¹⁰ Torr following bakeout [19].
RESULTS AND DISCUSSION

Surface Chemistry of Lubricant Additives

The reactive properties of simple chlorinated hydrocarbons were measured using molecular beam methods in ultrahigh vacuum [16-18] by placing a capillary dosing source in front of the iron sample where the reflected flux was monitored as a function of sample temperature using a quadrupole mass spectrometer to measure reaction activation energies and gas-phase products. The resulting surface was analyzed using Auger or X-ray photoelectron spectroscopy. The results showed that simple chlorinated hydrocarbons (CH₂Cl₂, CHCl₃, CCl₄) completely thermally decomposed at the surface to deposit carbon and FeCl₂ and evolve gas-phase hydrogen. Sulfur-containing additives, dimethyl- and diethyl-disulfide, were examined using a similar strategy where reaction proceeds by the initial formation of methyl- and ethyl-thiolate species respectively.

The surface chemistry of more complex lubricant additives such as a phosphate or phosphite esters was examined on an iron oxide surface using temperature-programmed desorption (TPD) and surface spectroscopies [22,23].

Tribological Properties of Solid Lubricant Films

In order to understand the frictional properties of the reactivity formed films in greater detail, thin halide layers were evaporated onto a substrate in ultrahigh vacuum. Initial experiments were carried out using alkali halides since these have relatively simple crystal structures and will not be reduced by the substrate.

Measurement of the friction coefficient of a KCl film deposited onto iron shows that the friction is substantially reduced by the presence of the halide film from ~2 for the clean surface to a minimum of ~0.27 when the film is present. The reduction occurs after ~40 Å of KCl has been deposited and the film thickness coincides with an increase in the contact resistance between the tribopin and the substrate. This suggests that the decrease in friction coefficient corresponds to the completion of the first monolayer of the halide on the surface.

In order to test this proposal, the amount of bare iron on the surface was measured by adsorbing deuterium, which is the shear strength at zero pressure and \( \alpha \) is a constant where \( \alpha = 0.14 \pm 0.02 \) for KCl. The value of \( S_0 \) is much more dependent on a precise knowledge of the contact area and yields a value between 40 and 60 MPa.

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REFERENCES