

The surface and tribological chemistry of chlorine- and sulfur-containing lubricant additives

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Abstract

A model for the operation of chlorinated hydrocarbon extreme-pressure additives is outlined in which the chlorinated hydrocarbon thermally decomposes at the hot (~1000 K) interface forming a chloride + carbon film, which is simultaneously worn from the surface. Assuming that seizure occurs when the chloride film thickness decreases to zero reproduces the experimentally measured seizure load vs. additive concentration results. A similar model is found to apply to sulfur-containing additives. The thermal decomposition of model chlorinated hydrocarbons is investigated in ultrahigh vacuum (UHV) using constant-flux molecular beams and reveals that these react with similar activation energies as at higher pressures, forming films of identical compositions to those found tribologically. This allows the surface reaction chemistry of model extreme-pressure additives and the tribological properties of the films to be investigated separately in UHV. In this vein, measurements of the tribological properties of thin KCl films grown on iron in UHV show that the friction coefficient drops from a clean-surface value of ~1.9 to ~0.27 after completion of the first monolayer.

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1. Introduction

Commercial lubricants, required to operate under severe conditions, are comprised of several components. The most abundant of these is the base fluid, which may be a mineral oil or, in some cases, water. The lubricants are ‘formulated’ by adding various components. Some of these function, for example, to stabilize the fluid against oxidation or biological decay. Others improve the tribological performance. The key parameter in understanding the properties of these reactive additives is the temperature of the interface, since an increase in temperature of the rubbing surfaces correspondingly increases the rate at which the tribological film is formed. This paper therefore focuses on understanding the way in which these lubricant additives react at the tribological surface, the nature of the film that is formed and the role of this film in improving tribological behavior. This improvement may be in the reduction of friction, in allowing an

increase in the loads that can be sustained or in generally providing a protective coating on the surface. Fully understanding these phenomena requires the synthesis of mechanical approaches with an understanding of the chemical and physical properties of the interface, and therefore requires a truly interdisciplinary strategy; this paper focuses on an area where it has been well established that surface chemical reactivity plays a key role in forming tribological films, that of extreme-pressure (EP) lubricants which are used for processes such as machining, wire drawing, fineblanking, etc. A wide range of compounds has been claimed to be effective extreme-pressure additives, but the ones that are currently most commonly used generally contain chlorine, sulfur or phosphorus [1–9]. These are most often added as organic compounds, which render them soluble in the base lubricating fluid. Since many of the compounds that are currently used for this purpose are either environmental pollutants or health hazards, or both, these will ultimately have to be replaced by more benign alternatives [10]. Since these additives are understood to thermally decompose at the lubricated interface, the nature of this interface is of crucial relevance to understanding the behavior of the additive. This means that the

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additive + surface combination must be considered as a whole since the lubricant film is formed by a chemical reaction between them. This clearly means that what may be a good lubricant additive for one metal may not be such a good additive for another. In addition, the presence of surface contaminants, for example oxide films or carbonaceous layers, can profoundly affect the reactivity at the surface. This problem is, to some extent, obviated in the extreme-pressure regime since wear rates are usually sufficiently high that these surface contaminants are worn away.

2. Measurements of interfacial temperatures

Previous observations that melting occurs at the interface when the average surface temperature, T , reaches the melting point at the interface can be exploited to measure interfacial temperatures at high loads and in situations in which the thermo-emf cannot be measured [11]. This has been done using a conventional pin and v-block apparatus in which the pin was made of a material of known melting point. The wear rate was measured as a function of the applied load where it is anticipated that the wear rate will become exceedingly large as the interfacial temperature approaches the melting point of the lowest melting point material, as suggested above. The results of wear rate vs. applied load for a copper pin sliding against steel is shown in Fig. 1 [11]. This indeed shows a rapid increase in wear rate, and the asymptote in this curve is taken to be due to the interfacial temperature reaching the melting point of copper. These data can be analyzed in greater detail. From first principles, it is assumed that $(T - T_0) \propto W$, where T_0 is the ambient temperature and W the load.

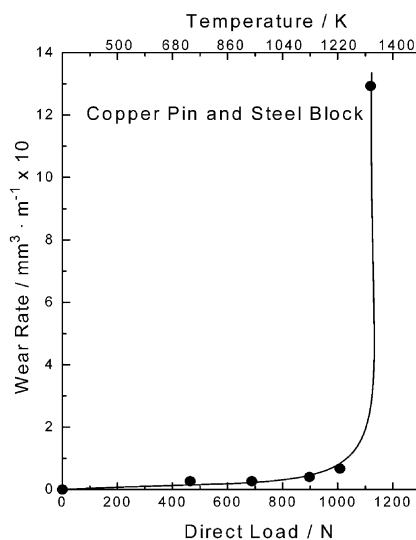


Fig. 1. Plot of wear rate vs. load using a copper pin.

Archard has suggested that the wear rate R depends on W and interfacial shear strength S as [12,13]

$$R \propto W/S \quad (1)$$

The shear strength has also been shown to be temperature dependent such that:

$$S \propto \ln(T_m/T) \quad (2)$$

so that as $T \rightarrow T_m$, $S \rightarrow 0$ [14]. From Eq. (1), this yields the large wear rate as the interfacial temperature approaches the melting point. The line shown plotted through the data of Fig. 1 is a theoretical plot from Eqs. (1) and (2), where the agreement with the experimental data is very good. This method allows one to calibrate the interfacial temperature during the pin and v-block experiment. This apparatus is particularly well suited to studying extreme-pressure additives since the loads are sufficiently high that it operates in the extreme-pressure régime and also allows the interfacial temperature to be measured. As noted above, it does not measure the 'flash' temperature, but an average temperature at which a physico-chemical change (in this case, surface melting) takes place. It is likely that this is also a reasonable measure of the temperature that controls the rate of chemical reaction at the surface.

3. Model for extreme pressure lubrication

The extreme-pressure effectiveness of various simple model lubricant additives was measured from the seizure load as a function of additive concentration and the results are displayed in Fig. 2.

This reveals that the addition of a small amount of chlorinated hydrocarbon substantially increases the seizure load. Two types of behavior are observed. The first is exemplified by methylene chloride (CH_2Cl_2) and chloroform (CHCl_3), which show a plateau with increasing chlorine concentration and the second is exemplified by carbon tetrachloride (CCl_4), where the seizure load

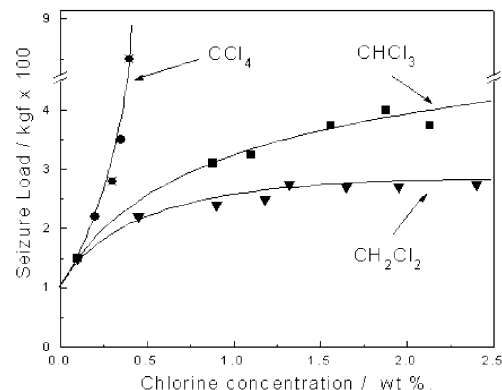


Fig. 2. Plot of seizure load vs. additive concentration for a range of small chlorinated hydrocarbons dissolved in poly α -olefin.

continues to increase. Analysis of the surface reveals the formation of an iron chloride [15].

3.1. Wear rate during rubbing

Wear rates for steel pins in a model lubricant comprising methylene chloride dissolved in a poly α -olefin can be measured in the same way as shown in Fig. 1 and the results of wear rate vs. load are plotted in Fig. 3. This shows that the wear rate increases with applied load. Using the temperature calibration from Section 2 reveals that the asymptote in this curve corresponds to a surface temperature of ~ 920 K, close to the melting point of FeCl_2 (943 K).

3.2. Film growth rate measurements and a model for extreme-pressure lubrication

The rate of film growth due to the thermal decomposition of methylene chloride on iron was measured using a microbalance. In this case, the film thickness is measured as a function of temperature and pressure, from the change in mass of the iron foil sample as a function of time [16]. The film thickness X at any point during a tribological experiment can then be calculated from the difference between the rates of film growth, r_g and wear rate, r_r :

$$dX/dt = r_g - r_r \quad (3)$$

where X represents the thickness of the FeCl_2 film. Since this film is proposed to act as a solid lubricant, seizure is suggested to occur at the load at which the film thickness decreases to zero. Eq. (3) is solved using the indepen-

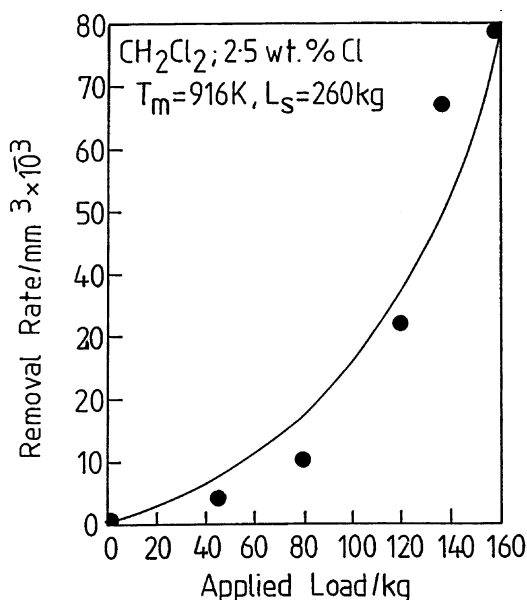


Fig. 3. Plot of wear rate vs. applied load for methylene chloride dissolved in a poly α -olefin.

dently measured values of r_g and r_r and the results are displayed in Fig. 4 and compared with the experimental data from methylene chloride taken from Fig. 2.

Clearly the agreement between the experimental data and the calculations is extremely good, indicating that the chlorinated hydrocarbon extreme-pressure additive thermally decomposes at the hot iron surface to form an FeCl_2 film which prevents seizure. This film is simultaneously worn from the surface and seizure occurs when the film is completely worn away. In this case, the plateau arises naturally in the model because, at these loads, the surface approaches the melting point of the tribological (FeCl_2) film and so is extremely rapidly worn from the surface.

Similar experiments using sulfur-containing additives (dimethyl disulfide, diethyl disulfide, carbon disulfide) show that these similarly thermally decompose on the surface to yield an FeS film [17].

4. Tribochemical reactions in ultrahigh vacuum

In order to explore the tribological chemistry of chlorinated hydrocarbons further and, in particular, to follow the nature of any gas-phase products, molecular beam experiments have been carried out in ultrahigh vacuum [18].

These experiments were carried out using an atomically clean iron foil in ultrahigh vacuum. A capillary was placed so that a constant flux beam of the chlorinated hydrocarbon was incident on the iron surface and the gas-phase products detected using a quadrupole mass

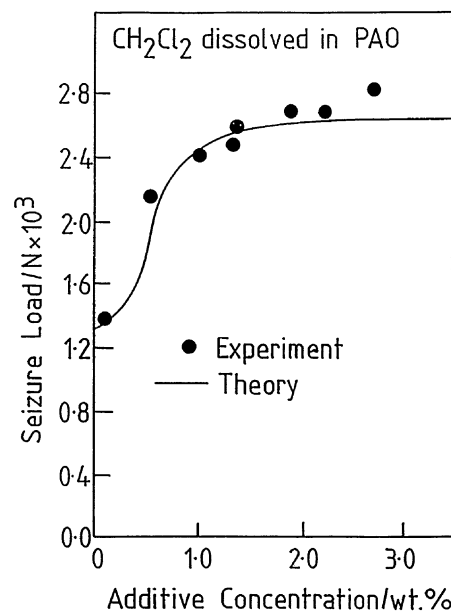
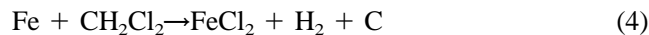
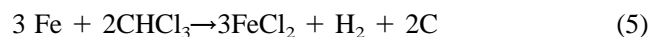


Fig. 4. Comparison between experiment and theory for the seizure load vs. concentration for methylene chloride dissolved in poly α -olefin.

spectrometer also placed in front of the iron sample. The nature of the surface could also be monitored using Auger spectroscopy. Typical results for methylene chloride incident on a clean iron surface are shown in Fig. 5. In this case, the reflected methylene chloride flux (\circ) decreases as the sample temperature increases indicating reaction with the surface. The deviation of this curve from the horizontal is proportional to the rate of methylene chloride reaction with the surface and can be used to calculate the reaction activation energy and leads to a value of 9.5 ± 0.5 kcal/mol. This value is in excellent agreement with the reaction activation energy measured at higher pressures using a microbalance and indicates that similar reaction pathways are probed in both regimes [16]. Furthermore, an analysis of the surface following reaction reveals the presence of FeCl_2 in accord with results collected at higher pressures and in tribological experiments. This indicates that a similar tribological film is deposited in ultrahigh vacuum and that the surface reaction chemistry is identical. Hydrogen is the only other gas-phase product detected from the reaction between methylene chloride and the surface (\bullet) and the increase in hydrogen formation rate exactly mirrors the decrease in methylene chloride signal. This indicates that the surface reaction is given by:



where the carbon is present in the form of small carbonaceous particles. Similar molecular beam experiments with chloroform [19] and carbon tetrachloride [20] show that their reaction activation energies are identical to those measured using the microbalance at higher pressures. The surface reactions for these chlorinated hydrocarbons are given by:



and

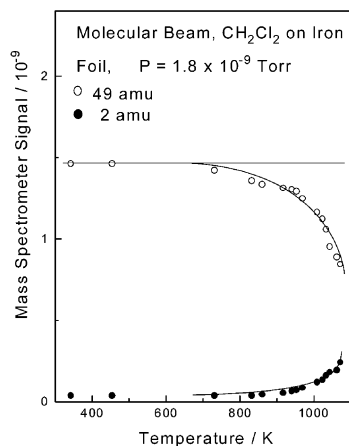


Fig. 5. Plot of reflected methylene chloride and hydrogen flux from clean iron as a function of temperature.

Thus, the ratio of FeCl_2 to carbon in the tribological film simply reflects the stoichiometry of the reactant chlorinated hydrocarbon. In particular, a film formed using carbon tetrachloride has the highest halide to carbon ratio of all of the chlorinated hydrocarbons. It is evident from the data in Fig. 2 that carbon tetrachloride is the most effective EP additive and this effect has been traced to its ability to form an iron carbide [21]. Thus, in this case, when the halide is removed from the surface, the carbide acts as an effective anti-seizure film. The diffusion of carbon into the iron bulk can be monitored using Auger spectroscopy by measuring the amount of carbon remaining on the surface after heating to various temperatures. The following experiment was therefore carried out. A clean iron sample was saturated with either methylene chloride or carbon tetrachloride at a sample temperature of 300 K in ultrahigh vacuum. The initial coverage of carbon on the surface was monitored using Auger spectroscopy. The sample was then heated to some higher temperature for a period of 5 s and the amount of carbon remaining on the surface again monitored using Auger spectroscopy. Since no carbon-containing species are found to desorb from the surface, any loss of carbon must therefore be due to carbon diffusion into the bulk of the sample to ultimately form a carbide. The results of this experiment are displayed in Fig. 6.

The initial carbon coverage from methylene chloride (\bullet) is larger than that for carbon tetrachloride (\blacksquare) due to the different carbon to chloride ratios in these chlorinated hydrocarbons. As the sample is heated, the amount of carbon on the surface decreases due to diffusion into the iron. This occurs at ~ 600 K for carbon deposited from carbon tetrachloride and ~ 750 K for carbon deposited from methylene chloride, in accord with the

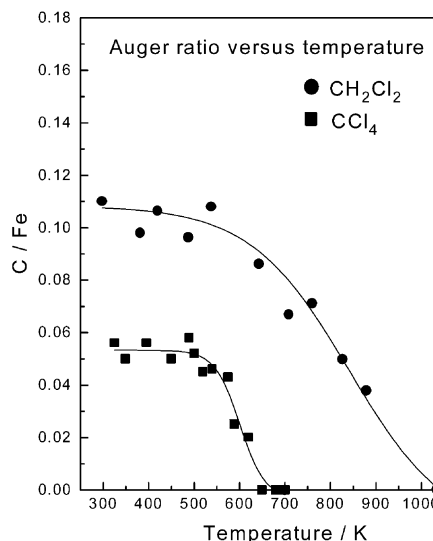


Fig. 6. Plot of carbon coverage as a function of annealing temperature.

tribological properties. An explanation for this effect is that both carbon and chlorine bond to the surface by accepting electrons from the metal so that co-adsorbed chlorine will have the effect of decreasing the heat of adsorption of the carbon, thereby lowering the activation energy for diffusion into the sample bulk.

These results show that the films deposited by reaction on to a clean iron surface are identical to those formed during extreme-pressure lubrication. This allows the tribological properties of the extreme-pressure films to be probed in ultrahigh vacuum to explore how the film structure affects its tribological properties. In order to understand the relationship between the structure and thickness of the film and its tribological properties, we have examined the frictional behavior of thin halide films deposited on to clean iron in ultrahigh vacuum.

5. The frictional properties of thin halide films

Thin potassium chloride films were deposited on to clean iron in ultrahigh vacuum using a small alumina tube furnace filled with KCl. Film thicknesses were measured either using a quartz crystal microbalance or from the relative intensities of the potassium, chlorine and iron X-ray photoelectron signals and electron escape depths [22]. In the latter case, the film thickness was measured assuming that the KCl film grew uniformly on the surface. This resulted in film thicknesses that considerably underestimated those measured by the microbalance suggesting that the films did not grow uniformly. This conjecture was confirmed by measuring the amount of bare iron surface using deuterium after depositing various thicknesses of KCl. Since deuterium only adsorbs on to the bare iron, but not on to KCl [23], the amount of hydrogen on the surface is an effective measure of the amount of exposed bare metal and this reveals that the iron is not completely covered until ~ 40 Å of KCl had been deposited, as determined using a quartz crystal microbalance.

The friction coefficient of the thin KCl film was measured using a tungsten carbide tribopin [22] as a function of film thickness and decreased rapidly from the clean iron value of ~ 1.9 to ~ 0.27 after the deposition of ~ 40 Å of KCl and then remained rather constant with the addition of up to 2000 Å of KCl.

It is proposed that the initial drop in friction coefficient coincides with the completion of the first monolayer [22]. Confirmation of this idea came from a measurement of the contact resistance, which maintained a low value for film thicknesses below ~ 40 Å, and started to rise for thicker films. It was further assumed that the friction coefficient at intermediate coverages was proportional to the relative coverages of the KCl film and bare iron surface [22] so that, writing the first-layer coverage of KCl as Θ_{KCl} where $0 < \Theta_{\text{KCl}} < 1$,

$$\mu = \mu_{\text{KCl}}^0 \Theta_{\text{KCl}} + \mu_{\text{Fe}}^0 (1 - \Theta_{\text{KCl}}) \quad (7)$$

where μ_{KCl}^0 is the friction coefficient of the KCl monolayer, and μ_{Fe}^0 is the friction coefficient of clean iron with the slider. Assuming that the rate of KCl adsorption on to the bare metal in the first layer is proportional to the area of the exposed metal surface yields a rate of adsorption proportional to $1 - \Theta_{\text{KCl}}$, via Langmuir kinetics [24], gives by integration:

$$\Theta_{\text{KCl}} = 1 - e^{-\alpha t} \quad (8)$$

where α is a constant. Substituting Eq. (8) into Eq. (7) yields:

$$\mu - \mu_{\text{KCl}}^0 = (\mu_{\text{Fe}}^0 - \mu_{\text{KCl}}^0) e^{-\alpha t} \quad (9)$$

Since the film thickness is proportional to the deposition time, Eq. (9) also represents the theoretical change in friction coefficient as a function of film thickness. The friction coefficient data are replotted in Fig. 7 as $\mu - \mu_{\text{KCl}}^0$ vs. film thickness t (■), where μ_{KCl}^0 is taken to be 0.27 ± 0.03 . In cases where more than one measurement of the friction coefficient was made for the same KCl film thickness in different runs, these values have been averaged and the resulting error bars included on the figure. A best fit to Eq. (9) yields a value of $\alpha = 0.39 \pm 0.02 \text{ \AA}^{-1}$. The corresponding KCl coverage in the first layer from these tribological data is given by Eq. (8) and shown plotted as a solid line on this graph. This reveals that the predicted first layer film thickness saturates when a total film thickness of ~ 40 Å has been deposited. It should be emphasized that this just represents the coverage of the first layer, and that second and subsequent layers are being formed at the same time. The first-layer KCl coverage was also measured using deu-

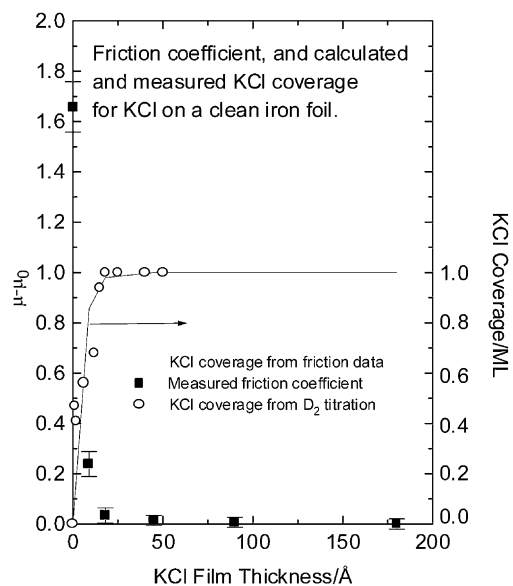


Fig. 7. Plot of friction coefficient vs. film thickness (■), the predicted first monolayer coverage (solid line) and the corresponding value measured by deuterium titration (○).

terium titration as outlined above and values are also plotted in Fig. 7 (○). Clearly the agreement between these measurements and the KCl coverage predicted from the tribological data is extremely good. Thus, direct measurements of the first-layer KCl coverage are in accord with the contact resistance measurements indicating that the friction coefficient is well represented by Eq. (7).

These results reveal that the first monolayer is essentially complete when a film of ~40 Å has been deposited, and that bare surface is present for lower coverages while, simultaneously, second and subsequent layer growth has started. The kinetic data can be used to estimate the thickness of the first-layer KCl film [25]. The film growth data can be analyzed by assuming that KCl grows in each of the layers with identical kinetics as that in the first layer and that each of the layers have identical film thicknesses and that the sum of the layer thicknesses equals the total thickness of the film. Using these assumptions, it can be shown that $t_0 = 1/\alpha$ [25]. From above, $\alpha = 0.39 \pm 0.02 \text{ \AA}^{-1}$ giving $t_0 = 2.6 \pm 0.2 \text{ \AA}$. The face-centered-cubic unit cell dimensions for KCl are 6.29 Å, equal to a bilayer KCl film thickness if the (100) face is oriented parallel to the surface. A monolayer K plus Cl film would be half this value (3.15 Å), in reasonable agreement with the thickness measured from the tribological and deuterium blocking data ($2.6 \pm 0.2 \text{ \AA}$). Clearly, this is an approximate value since it relies on the assumptions that all of the layers have an identical thickness, and that the adsorption kinetics into each layer are identical.

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