

The surface chemistry of chlorinated hydrocarbon extreme-pressure lubricant additives

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Chlorinated or sulfurized hydrocarbons are commonly added to a base fluid to synthesize lubricants used under extreme-pressure (EP) conditions. It has been demonstrated that the interfacial temperature in the EP regime varies linearly with the applied load and that temperatures in excess of 1000 K can be attained. At these temperatures, both microbalance experiments carried out at high pressure as well as molecular beam experiments performed in ultrahigh vacuum reveal that chlorinated hydrocarbons thermally decompose forming a film that consists of a layer of iron chloride and which can also incorporate small ($\sim 50 \text{ \AA}$ diameter) carbon particles. These particles may affect the coefficient of friction of the film. The lubricant fails and seizure takes place when the film is removed sufficiently rapidly for metal–metal contact to occur so that EP lubrication is described as a dynamic phenomenon. Under appropriate circumstances, sufficient carbon can be incorporated into the iron substrate that it becomes a carbide. In this case, seizure is prevented even when the halide layer is removed because of the hardness and high melting temperature of this carbide. Ultrahigh vacuum experiments also suggest that carbon diffusion into the iron and presumably also ultimately carbide formation, is facilitated by co-adsorbed chlorine which may then explain the excellent extreme-pressure properties of carbon tetrachloride. Finally, a similar tribological model is successfully applied to dimethyl disulfide where, in this case, FeS forms the anti-seizure layer.

Keywords: extreme-pressure lubrication, interfacial temperature, chlorinated hydrocarbons, dimethyl disulfide, seizure load, molecular beam experiments, surface composition, X-ray photoelectron spectroscopy, Raman spectroscopy

1. Introduction

Extreme-pressure lubricants are used in a wide range of machining and other metalworking applications, and generally consist of a base lubricating oil mixed with other ingredients (additives) [1–7]. Perhaps the chemically simplest, as well as most economically efficient class of extreme-pressure (EP) additives in common use, those containing chlorine, have been investigated in detail. Experience has shown that chlorinated hydrocarbons appear to be irreplaceable in many very heavy duty operations, such as severe stainless-steel metal working and forming brake drums or fineblanking heavy parts for the auto industry. For many manufacturers, this class still represents the greatest tonnage of EP lubricant additive utilized. Recent recycling and various handling improvements have addressed most environmental concerns associated with the use of these compounds. There, however, still remains significant motivation to find environmentally more benign alternatives. The following investigates the chemical processes by which these extreme-pressure lubricants operate. It is shown that rather high temperatures ($\sim 900 \text{ K}$) can be attained at the tribological interface [8] causing reactive formation of an anti-seizure film which, depending on tribological

conditions and therefore interfacial temperature, may consist of an iron chloride [9–13] or iron carbide [14,15] when chlorinated hydrocarbons are used and FeS when using dimethyl disulfide. Since this layer is continually removed during extreme-pressure lubrication, such a *reactively* formed film can continue to act as a lubricant even under these conditions.

2. Experimental apparatus

A number of pieces of experimental apparatus were used in the course of this work which have been described in detail elsewhere [8,12]. Briefly, however, tribological measurements were made using the pin and v-block apparatus [16]. In this case, the pin and v-blocks were immersed in the model extreme-pressure lubricant which consists of a chlorinated hydrocarbon dissolved in a poly α -olefin. The whole apparatus could be enclosed in a nitrogen-filled glove bag. The pin was rotated, while clamped between the v-shaped blocks and both the applied load and the torque required to rotate the pin at a constant angular velocity can be monitored simultaneously. As the applied load increased, the torque increased correspondingly, the slope of the curve of torque versus load yielding the interfacial coefficient of friction. When the lubricant failed, a sudden rise in the

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torque was observed and the associated load was designated the seizure load.

Film growth kinetics due to the decomposition of chlorinated hydrocarbon vapors on an iron surface were measured using a microbalance which can continually monitor the change in sample mass as a function of time. This mass change is taken to be proportional to the thickness of the film reactively deposited onto the iron foil. The operation of this apparatus is discussed in detail elsewhere [17].

Experiments were also carried out in a stainless-steel, ultrahigh vacuum chamber consisting of a 12"-diameter chamber that operates at $\sim 5 \times 10^{-11}$ Torr following bakeout and which was pumped by a combination of ion and sublimation pumps [18]. An iron foil (Aesar, 99.999%) was mounted to the end of a carousel geometry manipulator and could be heated to ~ 1200 K for sample cleaning. The chamber was equipped with a cylindrical-mirror analyzer that was used for Auger analysis of the sample and a quadrupole mass spectrometer which was used for residual gas analysis and monitoring products evolved by chemical reactions with the surface. The chlorinated hydrocarbon molecular beam was generated by leaking the reactant via a variable leak valve through a 1 mm internal diameter capillary that was incident at $\sim 70^\circ$ to the normal onto the iron foil sample, while the sample was simultaneously located in front and in line of sight of the ionizer of a quadrupole mass spectrometer which was used to detect reaction products.

Various tools were used to probe the nature of the tribological films formed on the surfaces of the pins, v-blocks or on the iron foil from the microbalance experiments. These included X-ray photoelectron spectroscopy to monitor the nature and oxidation state of the surface, Auger spectroscopy for surface analysis, Raman spectroscopy to probe the bulk nature of reactively formed films and Mössbauer spectroscopy to examine the chemical nature of the iron in the samples.

3. Results and discussion

Figure 1 shows the results of experiments carried out using the pin and v-block apparatus plotting the seizure load versus the additive concentration with methylene chloride (CH_2Cl_2), chloroform (CHCl_3), hexachloroethane (C_2Cl_6) and carbon tetrachloride (CCl_4) as lubricant additives. Note that the concentrations are normalized to chlorine concentration for each additive. Two general types of behavior are found. The first is exemplified by methylene chloride and chloroform where the seizure load initially increases with additive concentration but reaches a plateau after a certain concentration. Note that the seizure load in the plateau region is different for the two additives and this effect will be discussed in detail below. In complete contrast to this behavior, the seizure load continues to increase

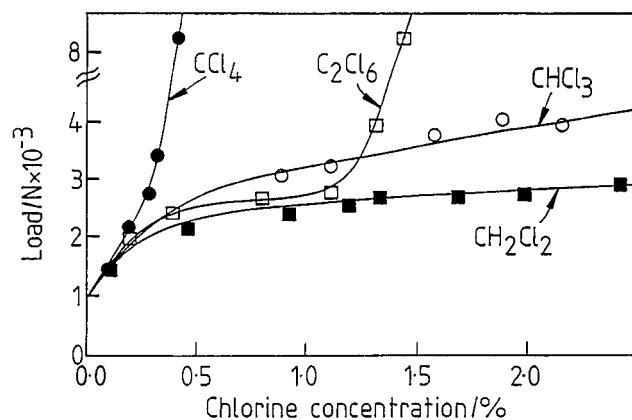


Figure 1. Plot of seizure load versus additive concentration measured in wt% chlorine for a series of chlorinated hydrocarbons dissolved in a poly α -olefin using a pin and v-block apparatus.

without showing any sign of forming a plateau when carbon tetrachloride is used as an additive. Experiments were stopped at ~ 0.4 wt% chlorine concentration in this case since this corresponded to the highest load attainable using the pin and v-block apparatus. C_2Cl_6 displays both types of behavior exhibiting a plateau below ~ 1.2 wt% but with a seizure load that increases dramatically above that concentration. Analysis of the material removed during the tribological experiment (figure 2), in this case by comparison of the X-ray photoelectron spectrum of the Cl 2p region with model compounds, reveals the presence of an halide. It has been shown that the temperature at the interface between the pin and the v-block can be measured and is given, for the experimental configuration used, as:

$$T = T_0 + \alpha L, \quad (1)$$

where T_0 is the bath temperature and α is a constant. The constant α can be measured for the pin and v-block apparatus if the interfacial material and its melting point are known since the wear rate becomes asymptotically infinite when the interfacial temperature reaches the melting point of the material at the interface (figure 3). This yields a value of α when using methylene chloride as additive with steel pins of 0.25 ± 0.02 K/N [8,19]. That is, the interfacial temperature rises by ~ 2.5 K for each kgf applied to the v-blocks. This means that temperatures up to and above ~ 1000 K can be attained at the interface [20,21].

Film growth kinetics were measured for various model chlorinated hydrocarbon additives using the microbalance and typical results are shown in figure 4 for the variation in films thickness as a function of time. Similar experiments as a function of temperature and pressure allow the film growth kinetics to be measured in detail. Analysis of the films formed from methylene chloride shows the formation of an iron halide and the Raman spectrum of the film (figure 5) shows peaks at

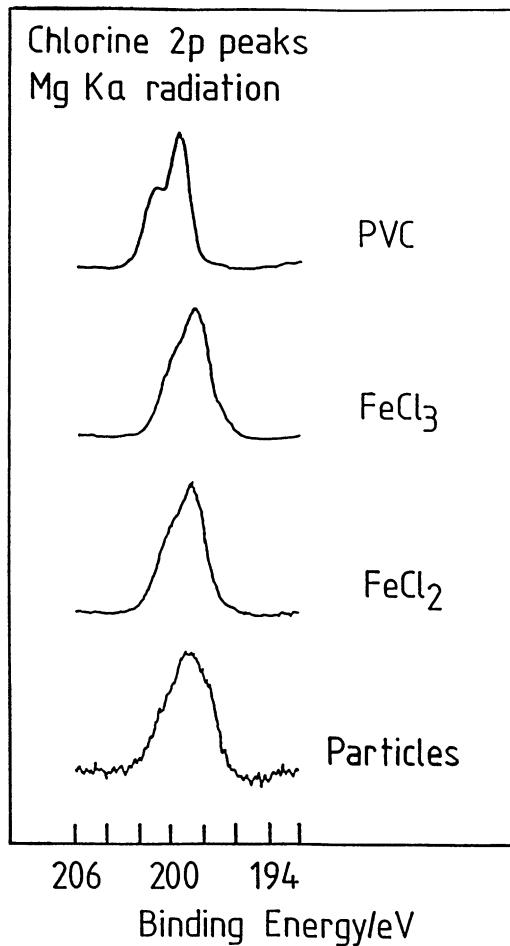


Figure 2. Cl 2p X-ray photoelectron spectrum of wear particles removed during lubrication by a chlorinated hydrocarbon additive compared with FeCl_2 , FeCl_3 and polyvinylchloride.

1350 ± 10 and $1600 \pm 10 \text{ cm}^{-1}$ characteristic of the presence of small carbonaceous particles in the film. A more careful analysis of this spectrum suggests that the carbonaceous particles are $\sim 50 \text{ \AA}$ in diameter [9,10,17]. Note that the Raman spectrum of the film formed from CCl_4 shows no such graphitic particle peaks.

In addition to films being reactively formed at the surface, they are simultaneously removed due to the rubbing action of the pin against the v-block. The rate of material removal can be measured from the width of the wear scar formed on the surface of the v-blocks [17] to yield data similar to that displayed in figure 3. The asymptotic load found when using methylene chloride as additive is $\sim 2.5 \times 10^3 \text{ N}$ [12]. Substitution of this value into eq. (1) shows that the interfacial temperature at this load is $\sim 920 \text{ K}$ which corresponds well to the melting point of FeCl_2 (940 K [24]). This observation is in accord with surface analysis data both of the pins and v-blocks as well as the iron foils all of which show the presence of a surface halide. This implies that the maximum sustainable load corresponds to the maximum sustainable surface temperature of the lubricating interface which, in this case, is the melting point of an iron halide. Thus, at this

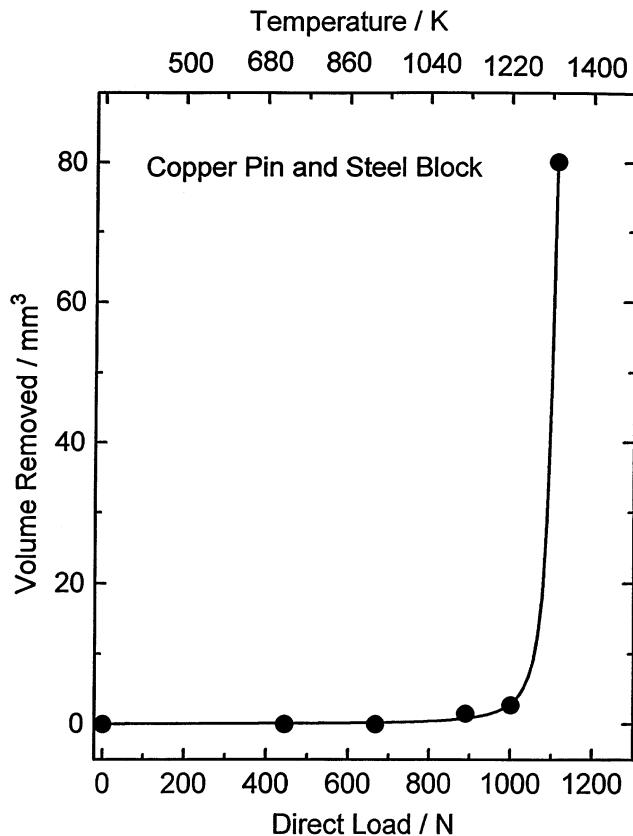


Figure 3. Plot of wear rate versus applied load collected in the pin and v-block apparatus measured using a copper pin and steel v-blocks. The temperature scale at the top is calibrated by taking the asymptote to correspond to the melting temperature of copper [19].

temperature the lubricating film melts and the resulting liquid is very rapidly removed from between the contacting surfaces. These results can then be used to more quantitatively predict the seizure load versus additive concentration behavior shown in figure 1 by assuming that the interfacial film thickness X is given by:

$$\frac{dX}{dt} = r_g - r_r, \quad (2)$$

where r_r and r_g are the film removal and growth rates respectively, both of which are independently measured experimentally. It is assumed that seizure occurs when the lubricating film is removed (i.e., as $X \rightarrow 0$) and the result of this model calculation is shown in figure 6 compared with the experimental data for CH_2Cl_2 , where the agreement is good [17]. The plateau region arises naturally in this model since this load corresponds to an interfacial temperature at which the lubricating FeCl_2 film melts so that merely increasing the rate at which the film is formed by increasing the additive concentration has no beneficial effect since, irrespective of the film's thickness, all of the interfacial material is removed as it melts.

Similar film growth experiments can be carried out using chloroform (CHCl_3) and analyzed using XPS,

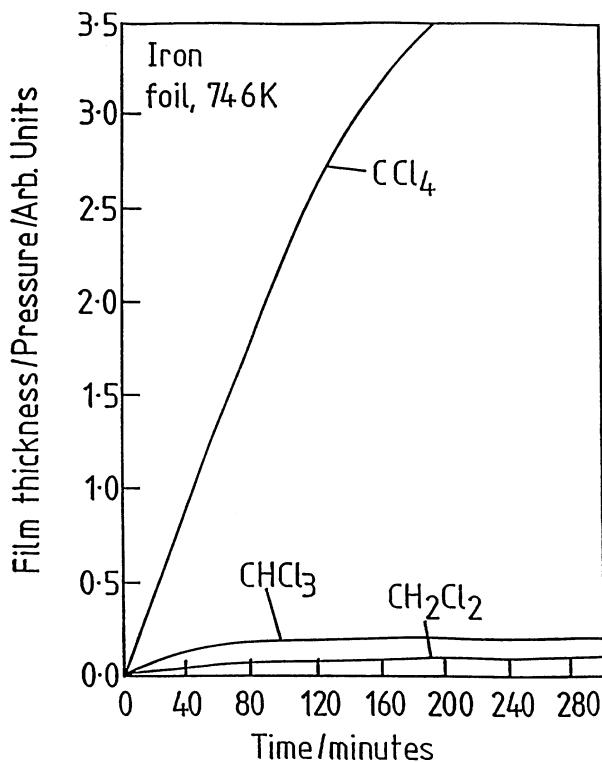


Figure 4. Plots of film thickness per unit pressure of additive measured using a microbalance from methylene chloride, chloroform and carbon tetrachloride vapor.

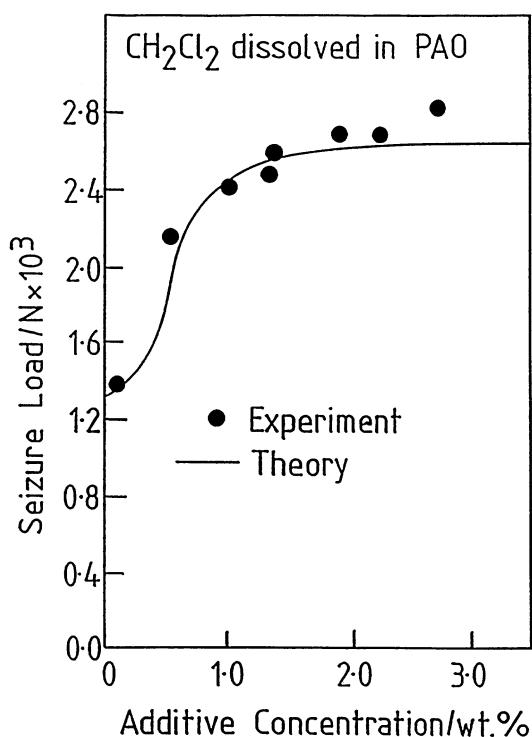


Figure 6. Experimental plots of seizure load versus additive concentration (●) for a model lubricant consisting of methylene chloride dissolved in poly α -olefin compared with the results of a theoretical calculation (—).

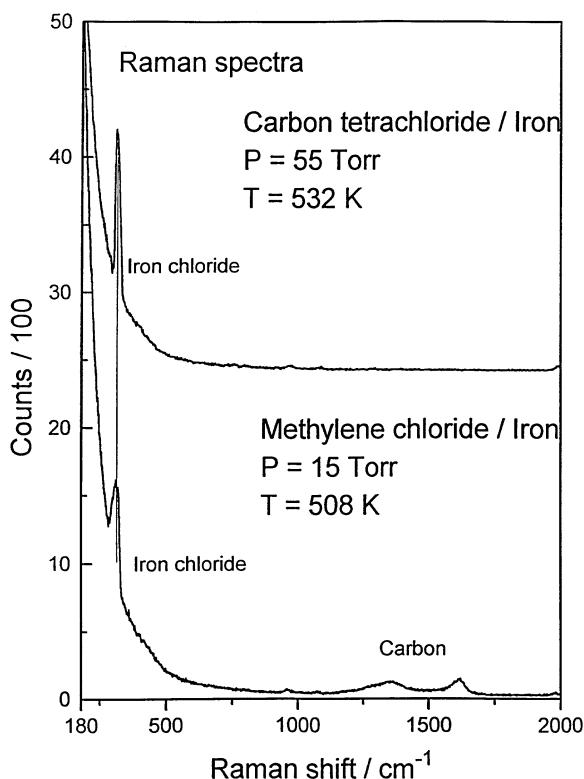


Figure 5. Raman spectra of the films formed on iron foils from the thermal decomposition of methylene chloride and carbon tetrachloride.

Auger and Raman spectroscopies reveal essentially identical film compositions consisting of an FeCl_2 layer incorporating small carbonaceous particles. The only difference between the two films is that slightly less carbon is incorporated into the film when chloroform is used than for methylene chloride. This suggests that the plateau found when using chloroform as a lubricant additive (figure 1) should correspond to the melting of an halide film. The seizure load at this point is, however, higher than for methylene chloride. The constant α in eq. (1) above is given by $\alpha = Kr\omega\mu$, where r is the radius of the pin, ω its rotational angular velocity, μ the interfacial coefficient of friction and K a constant that depends on the thermal conductivity of the region of contact between the pin and v-block [14,15,17]. This dependence of μ can easily be understood since the power dissipation at the surface that leads to the interfacial temperature rise will depend directly on this value. Indeed, the coefficient of friction when using chloroform as an additive is measurably lower than when methylene chloride is used ($(7.1 \pm 0.2) \times 10^{-2}$ compared with $((11 \pm 1) \times 10^{-2}$) and may depend on the concentration of carbon particles in the film. The temperature scale shown in eq. (1) can then be corrected for this value and the corresponding applied load at which the interfacial temperature reaches ~ 940 K calculated. The predicted seizure load range for chloroform calculated on this basis is displayed in figure 7 which replots the seizure load versus additive

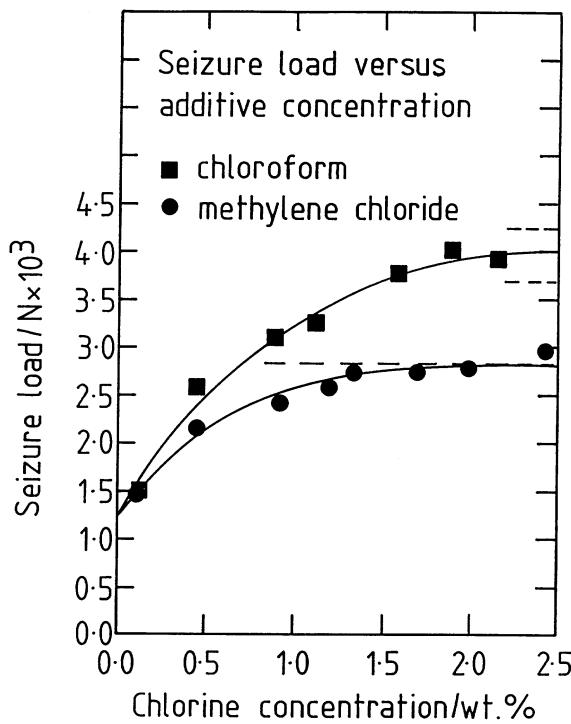


Figure 7. Plots of seizure load versus additive concentration using chloroform (■) and methylene chloride (●) as additives. The dotted horizontal lines around the curve for chloroform indicate the expected plateau range when using chloroform as additive by correcting the interfacial temperature calibration for different coefficients of friction.

concentration data from figure 1. Also shown on this curve is the expected range of seizure loads in the plateau region for chloroform which is in good agreement with experiment [15].

When carbon tetrachloride is used as an additive, extremely high seizure loads are attained corresponding to temperatures substantially higher than the melting point of FeCl_2 implying that, at least at the higher loads, iron chloride no longer fulfills the function of an anti-seizure layer. In order to probe the nature of the anti-seizure layer in this case, the wear rate was measured as a function of applied load when using carbon tetrachloride as an additive. Note that asymptotes in this curve correspond to the melting of the anti-seizure film. The resulting data are shown in figure 8 which displays large increases in the rate of material removal as a function of applied load. The corresponding temperature scale, calculated from eq. (1) but corrected for interfacial coefficient of friction as was done for chloroform above, is shown as the top abscissa in the figure. It is evident that the first increase at an applied load of $\sim 4 \times 10^2$ kgf corresponds to an interfacial temperature of ~ 930 K suggesting that, similarly to when CH_2Cl_2 and CHCl_3 are used as additives, iron chloride forms the anti-seizure film. Another increase is noted at $\sim 7 \times 10^2$ kgf corresponding to a temperature of ~ 1480 K. This corresponds to the approximate melting/decomposition temperature

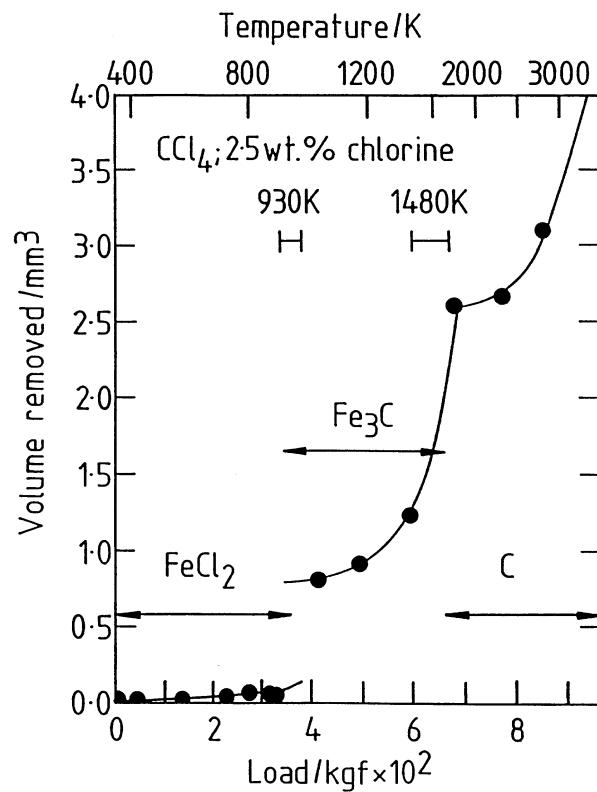


Figure 8. Plot of wear rate versus additive concentration when using carbon tetrachloride as additive. The top abscissa displays the interfacial temperature which has been corrected for coefficient of friction.

of iron carbide Fe_3C [24]. In order to further investigate the notion that a carbide might form the anti-seizure layer at high applied loads and interfacial temperatures, an iron foil was heated at various temperatures in CCl_4 vapor. The resulting Mössbauer spectra of the films deposited at various temperatures reveal that heating at 830 K in carbon tetrachloride produces a drastic change in the form of the spectrum which is characteristic of austenitic iron [25–27]. Heating at higher temperatures (1045 K) yields a spectrum characteristic of Fe_3C in accord with the tribological data presented above [14,28].

In order to probe the interfacial chemistry more carefully, d.c. molecular beam experiments were carried out in ultrahigh vacuum using atomically clean iron foils. In this experiment, a beam of methylene chloride effusing from a capillary doser is incident onto the sample which can be heated to various temperatures. The sample is also placed in front of a quadrupole mass spectrometer which allows the nature of any gas-phase reaction products to be monitored. The results of such an experiment are shown in figure 9 which plots the mass spectrometer intensity of hydrogen, the major reaction products as well as that of methylene chloride versus sample temperature. This indicates that the major gas-phase reaction product is hydrogen and an Arrhenius plot of the rate of hydrogen formation as a function of reaction

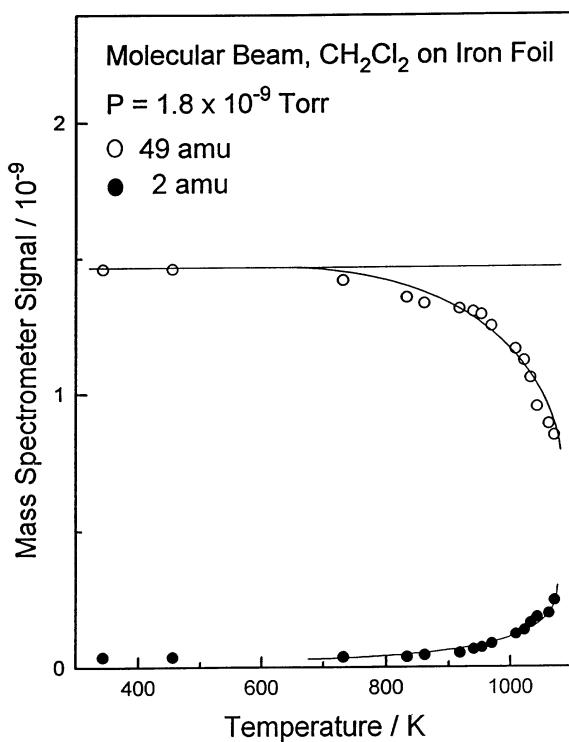
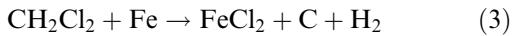


Figure 9. Methylene chloride (○) and hydrogen (●) fluxes measured as a function of sample temperature in ultrahigh vacuum resulting from a beam of methylene chloride incident on clean iron foil.

temperature gives an activation energy of 9.5 ± 0.9 kcal/mol, a value in excellent agreement with the film growth rate activation energy measured in the microbalance (9.7 kcal/mol). This suggests that methylene chloride reacts at the heated interface according to:



This stoichiometry is corroborated by the relative amounts of carbon found using Raman spectroscopy which agrees with the relative C : Cl ratios for CH₂Cl₂ and CHCl₃[10]. Note that the interfacial coefficient friction found when chloroform is used as additive is less than that found for methylene chloride, an effect that may be related to variations in the number of small carbonaceous particles incorporated into the film.

Molecular beam studies of chloroform and carbon tetrachloride decomposition on iron reveal similar chemistries where FeCl₂ is formed, carbon is deposited and, at least in the case of chloroform, hydrogen is evolved. A small amount of C₂Cl₄ is formed from carbon tetrachloride but the majority reacts to form a halide and carbon. Figure 10 shows the diffusion kinetics of carbon into iron, measured from the Auger intensity as a function of annealing temperature, after dosing the surface with methylene chloride or carbon tetrachloride. Clearly the carbon diffuses much more rapidly when co-adsorbed with four chlorines (from CCl₄) than when

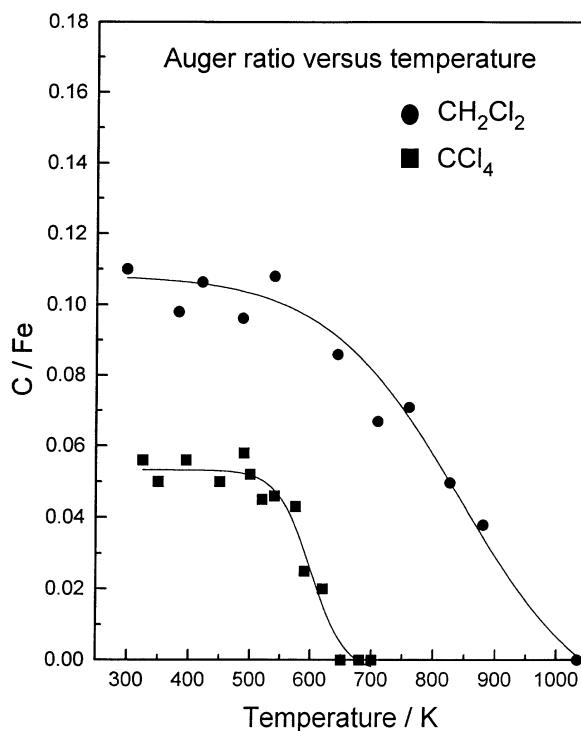


Figure 10. Plot of the carbon Auger signal ratioed to that of the iron substrate signal plotted versus sample annealing temperature following adsorption of methylene chloride (●) and carbon tetrachloride (■).

coadsorbed with two (when deposited from CH₂Cl₂). Since both carbon and chlorine adsorb onto transition-metal surfaces by accepting electrons from the substrate d-electron energy levels, they compete for electrons when co-adsorbed. This suggests that the heat of adsorption of carbon will decrease as the number of co-adsorbed chlorine atoms increases, thereby decreasing the activation energy for diffusion into the bulk of the iron and therefore accelerating the carbide-formation kinetics.

Finally, the seizure load versus additive concentration is plotted in figure 11 when using dimethyl disulfide as additive and shows a plateau-region seizure load of $\sim 4.1 \times 10^3$ N which then increases drastically for additive concentration above 7 wt% to exhibit a behavior similar to that seen for C₂Cl₆ (figure 1). Analysis of the nature of the film formed by thermally decomposing dimethyl disulfide vapor using XPS, Raman spectroscopy and X-ray diffraction reveals the formation of FeS [29]. Plotted on the right ordinate of figure 11 is the interfacial temperature measured from eq. (1) corrected for the interfacial coefficient of friction and shows that the plateau corresponds to an interfacial temperature of ~ 1470 K in good agreement with the melting point of FeS [24] and in accord with the model outlined above. The increase in seizure load at higher concentrations is probably due to the formation of iron carbide although this remains to be verified.

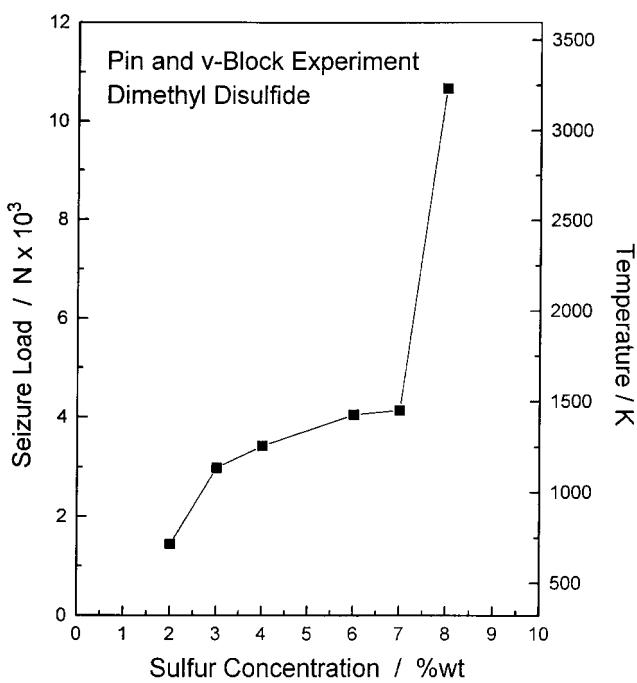


Figure 11. Plot of seizure load versus additive concentration for dimethyl disulfide dissolved in poly α -olefin measured using a pin and v-block apparatus. The temperature scale on the right-hand ordinate is calibrated for changes in coefficient of friction.

4. Conclusions

It is shown that chlorinated hydrocarbon additives can thermally decompose at the hot iron-based tribological interface to deposit anti-seizure films that consist of either $FeCl_2$ which incorporates small carbonaceous particles or Fe_3C , depending on the additive and temperature. This film is continually removed but also replenished by chemical reaction from the additive. Molecular beam experiments show that the additives completely thermally decompose and liberates predominantly hydrogen into the gas phase and the amount of chlorine on the surface modifies the carbon surface-to-bulk diffusion rate.

Finally, initial experiments using dimethyl disulfide as additive reveal the formation of an FeS film and that the presence of a similar plateau in the plot of seizure load versus additive concentration occurs at an interfacial temperature corresponding to the melting point of ferrous sulfide.

Acknowledgement

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