INFLUENCE OF TEMPERATURE ON TRIBOCHEMICAL REACTIONS OF HEXADECANE

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SUMMARY
This paper aims at investigating tribochemical reactions of n-hexadecane proceeding in a tribosystem lubricated by n-hexadecane at (i) ambient temperature, and (ii) elevated temperature. It is hypothesised that at ambient temperature reactions are mostly initiated by the mechanical action of the system and at elevated temperature (200°C) thermochemical reactions should be dominant. An experimental study was performed on a ball-on-disk machine with a steel-on-steel mating elements. To analyse wear tracks it was applied Infrared Microspectrophotometry (FTIRM) and Electron Spectroscopy for Chemical Analysis (ESCA/XPS). To investigate chemical changes of the bulk lubricant Gas Chromatography coupled with Mass Spectrometry (GC/MS) was applied. The obtained results provide clear evidence for the hypothesis that two types of oxygenation processes of n-hexadecane under boundary lubrication process should be considered. The first one at ambient temperature that is controlled by the mechanical action and the second one clearly controlled by temperature. The applied analytical techniques allowed to evidence the formation of two reaction product types from hexadecane under boundary lubrication conditions. These products include (i) products having Fe-O bonding (salts and chelates) and (ii) iron carbide.

Keywords: hexadecane, tribochemistry, thermochemical reactions, mechanochemistry, initiation of chemical reactions

1 INTRODUCTION
Early work on chemistry of boundary lubrication of steel by hydrocarbons, including hexadecane, demonstrated that the sliding behaviour of steel lubricated by hydrocarbons under boundary lubrication conditions could be related to chemical reactions at the sliding surfaces involving metal, hydrocarbon, and oxygen [1]. The results suggested that the reactions occur at sites where fresh metal surface was exposed by rubbing.

One of the basic questions in tribology is the mechanism by which anti-wear and extreme-pressure additives act to reduce wear and surface damage under boundary lubrication conditions. To study tribochemistry of these additives model base fluids have to be applied. Hexadecane is widely used as the model fluid for such experiments. Major compounds of lubricating base oils, namely hydrocarbons, undergo chemical changes during operation of tribological systems. In this case chemical reactions can be initiated by both temperature (thermochemical process) and mechanical action of the system (tribochemical process). The last ones can be specifically traced directly to the disrupted surfaces caused by the sliding contact generating surface active sites promoting reactions that otherwise may not occur.

Tribochemistry is generally referred to as the chemistry that occurs under rubbing conditions and producing molecular structures or interfacial layers that lubricate [2]. Reactions initiated by the mechanical action are distinguished as triboreactions and they can be initiated by the tribomission process [3]. All these specific physico-chemical processes lead to significant changes to occur on the surface and in the bulk oil. The latter changes lead to the lubricating oil deterioration.

To account for tribochemical reactions of hydrocarbons under boundary lubrication operating conditions, it is necessary to start such research using the most simple compounds, for example n-hexadecane, that is widely used as the low-viscosity model base oil [4-6]. Detailed analysis of specific products being formed at particular stages of the operation conditions may also allow to better understand detailed chemical processes proceeding both in the bulk lubricant and on the contact surfaces.

This paper aims at investigating tribochemical reactions of n-hexadecane proceeding in a steel-steel tribosystem lubricated by n-hexadecane at: (i) ambient temperature and (ii) elevated temperatures (200°C). It is hypothesised that at ambient temperature reactions are mostly initiated by the mechanical action of a tribological and at elevated temperatures thermochemical reactions should enhance dramatically reaction path ways initiated mechanically.

2 EXPERIMENTAL
2.1 Lubricant
n-Hexadecane (>99%, prod. Merck-Schuchardt) was used as a lubricant (model mineral base oil) without any additional purification.

2.2 Tribological tests
To investigate temperature affects on tribochemical reactions proceeding under boundary lubrication conditions in a steel-on-steel rubbing system, T-11 pin-on-disk tester was used. The tester (see Figure 1) was developed by the Institute for Terotechnology in Radom, Poland [7]. This apparatus allows to run tests at elevated
temperatures up to around 300 °C. It also continuously records the coefficient of friction and linear displacement due to wear. Elements of the friction pair (balls and disks) were made from 52100 bearing steel, 60 HRC. Before each run balls and disks were cleaned ultrasonically in hexane for 15 minutes.

All tests were performed under the following operating conditions: load 9.81 N; sliding velocity 0.25 m/s; sliding distance 500 m; ambient temperature 20 ± 2 °C and 200 ± 4 °C. After setting up the T-11 ball-on-disk tester and the test parameters, approximately 2 cm³ of hexadecane was placed in the disk-holding cup of the device. In the case of ambient temperature studies, the tests were performed immediately. In the case of 200 °C tests a software-controlled heating procedure was conducted prior to running the test. Disks after tests were hexane washed and stored above silica gel until further analysis.

Products of the tribochemical changes of n-hexadecane were investigated ex situ. To obtain detailed information concerning tribochemical changes of hexadecane, wear tracks of the tested disks were examined using selected analytical techniques (FTIRM, ESCA) allowing to investigate chemistry of products generated on the steel surface and the GC/MS technique to determine reaction products formed in the bulk hexadecane lubricant.

2.3 Analytical techniques

2.3.1 FTIR Microspectrophotometry

To investigate organic layer on wear tracks it was used i-series PE Fourier Transform Infrared Microspectrophotometer. Reflection spectra were recorded in the wavenumber range of 4000-700 cm⁻¹ with the resolution of 4 cm⁻¹ (64 scans at each point). All spectra were corrected by zapping of spurious band originated from carbon dioxide, near 2350 cm⁻¹ [8], as well as smoothing by Savitsky-Golay’s method and multipoint normalizing of baseline. The mathematical processing of spectra show no influence on their appearance.

2.3.2 Electron Spectroscopy for Chemical Analysis

In order to determine types of chemical bonds present in products layered on the disk steel surface, the wear track was subjected to ESCA/XPS analysis. Phi-5702 Multifunctional X-Ray Photoelectron Spectrometer with MgKα radiation source and binding energy of C 1s (284.6 eV) as the reference line. The energy resolution of high resolution spectra was ±0.2 eV. The Fe(2p), C(1s) and O(1s) profiles were recorded on φ 0.8 mm region at constant pass energy 93.9 eV. Ion sputtering of disk surface was carried out with argon ions of 3 keV energy. It was done at a glancing angle of 45° and depth profile was taken during 7 min sputtering.

2.3.3 Gas Chromatography/Mass Spectrometry

GC/MS technique was applied to identify products of the bulk lubricant chemical changes proceeding under the boundary friction conditions. It was performed by HP 5890 Series II Gas Chromatograph coupled with HP 5972 Series Mass Spectrometer under following conditions: injection 1 µl, column HP PONA (50 m, φ 0.2 mm), oven program 60 °C → 260 °C at 8°C/min, pressure program 100 kPa → 200 kPa at 4 kPa/min, flow rate 0.4 ml/min, carrier gas He 6.0.

3 RESULTS AND DISCUSSION

On the bases of the obtained results for the elevated temperature and previous results [9] relating to ambient temperature it is clearly demonstrated that tribochemistry of n-hexadecane is very significantly influenced by the elevated temperature that changes dramatically the oxidation process of this hydrocarbon. The chemically changed bulk lubricant at the temperature of 200 °C is composed of various oxygen-containing compounds, especially carboxylic acids (see Figure 2). Other oxygenated products are alcohols, aldehydes and ketons. They are typical chemicals of thermooxidation reactions proceeding under high temperature conditions.

The formed oxygenated compounds react with metal of the rubbing surfaces. Both the FTIRM and ESCA results suggest that reactions between the iron and carboxylic acids leads to formation of salts and/or chelates. Their characteristic infrared absorption bands (see Figure 3) around 3500-3000, 1740 and 1600 cm⁻¹ are different from those obtained at ambient temperature (see Figure 3a). In the latter case very specific absorption bands appear at around 1550 cm⁻¹, 1650 cm⁻¹ and 3300 cm⁻¹ [9].
Figure 3: FTIR spectrum of triboreaction products formed during friction process carried out at:
(a) elevated temperature (200 °C) and 
(b) ambient temperature (20 °C)

X-ray photoelectron spectroscopy is very sensitive to investigate not only the chemical composition, but also chemical environment of the element atom in a molecule. After running a survey profile on disk (see Figure 4), the regions for high resolution scan were selected.

Figure 4: ESCA survey profiles on steel disk lubricated by n-hexadecane during friction

Spectra of the iron, oxygen and carbon region revealed shifts in binding energy values due to chemical bonding. Figure 5 demonstrates that in spectra corresponding to external layers there are no signals coming from iron. In the further ones peaks appear at about 708 eV (Fe2p), 532 eV (O1s) and 284 eV (C1s).

In carbon photoelectrons region there are some overlapped signals at 288,3, 286,4 and 284,6 eV. Obtained results show that carbon might be at least in two forms, one Fe3C, another in oxygen-containing organic compounds with C=O bonding.

Table 1: Atomic concentration of elements in the film

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<thead>
<tr>
<th>Ion sputtering time (min)</th>
<th>Atomic concentration [%]</th>
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<tbody>
<tr>
<td></td>
<td>Fe2p</td>
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<tr>
<td>0</td>
<td>0</td>
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<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>20,32</td>
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<td>6</td>
<td>28,27</td>
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<td>7</td>
<td>28,10</td>
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Iron is the best candidate for electron donation, especially with increasing depth, indicating the formation of iron carbide Fe3C near to steel. The existence of large amount of carbon - determined using ESCA - and detection of organic compounds with FTIRM analysis clearly evidences that very specific tribochemical reaction layer in the disk wear track was formed. The layer consists of compounds including organic ligands and iron-oxygen bonding along with Fe-C bonding in the formed iron carbide (FeC3).

Figure 6 shows graphically the ESCA results demonstrating that reaction between the iron and carboxylic acids leads to formation of salts or chelates.
It is to note again at this point that their characteristic infrared absorption bands are different from those obtained at ambient temperature (see Figure 3).

4 CONCLUSIONS
Using a ball-on-disk tribometer under steel-on-steel boundary lubrication conditions, a study was made on tribochemical changes of n-hexadecane initiated by friction and enhanced by elevated temperature. This is a part of research on tribochemistry of lubricant base fluids. The use of the FTIRM and ESCA analytical techniques to analyse the surface films and deposits in the contact region allowed to evidence the formation of two reaction product types from hexadecane under boundary lubrication conditions. These products include (i) compounds having Fe-O bonding (salts and chelates) and (ii) iron carbide.

These results also provide an evidence for the hypothesis that two types of oxygenation processes of n-hexadecane under boundary lubrication process should be considered. The first one at ambient temperature that is controlled by the mechanical action and the second one clearly controlled by temperature. More research is needed to clarify the reaction mechanisms, particularly the mechanism of surface reactions.

5 REFERENCES