

Characterisation of monomolecular lubricant films

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SUMMARY

We studied the adsorption of two additives namely 8-hydroxyquinoline and ricinoleic acid from their solutions in toluene onto pure copper under noble gas atmosphere. After adsorption the samples were transferred into the X-ray photoelectron spectrometer, which was directly flanged to the adsorption vessel, without exposition to the environment. There angle resolved spectra of the C 1s, N 1s, O 1s and Cu 2p photoelectrons were recorded at analyser angles of 15°, 28°, 48°, 61°, 70° and 75°. The spectra showed that the adsorption of both additives took place under noble gas conditions. The binding of 8-hydroxyquinoline to copper resulted in a chemical shift of the 2p photoelectrons of the atoms at the surface, which equals the shift between pure copper and copper oxide. The thickness of the adsorbed ricinoleic acid layer was determined, using the straight line approximation, the density of the fluid and Seah and Dench's formula to calculate the inelastic mean free path. It showed that both additives adsorbed on the substrate formed a layer, which was less than a monolayer.

1 INTRODUCTION:

Additives play a major role in the formulation of new lubricants [1, 2]. They improve the quality and characteristics of base oils to match a wide spread variety of increasing demands [3]. Anti-Wear and extreme pressure additives are of main interest in boundary and mixed lubrication where solids were in contact. Adsorbed or chemisorbed molecules of these additives undergo chemical reactions and form wear reducing films on the surface of the solids in contact. In order to acquire knowledge of the behavior of the additives at the interface in these contacts, a fundamental understanding of the interaction of additive molecules with the surface of solids is needed. Knowing

the surface coverage, binding strength, orientation of the additive molecules and depth distribution of the elements is a prerequisite for the development of models of tribological systems.

ESCA is the appropriate analytical method for the chemical analysis of adsorbates on surfaces. No other analytical technique is capable of providing concentration depth profiles of organic compounds adsorbed to solid surfaces as well as of characterizing the binding of the molecules to the surface [4]. The chemical shift of the photoelectron peaks provides information of the atoms bound to the surface and is an indicator for the strength of the interaction between surface and additive. Angle resolved ESCA is capable of determining the depth distribution of elements in

each particular oxidation state in the first atomic layers. Moreover, the surface coverage can be deduced from the intensity dependent on the take off angle of the photoelectrons. At last, quantitative information about the composition can be gathered and quantitative concentration depth profiles are available.

In this study the adsorption of ricinoleic acid and 8-hydroxyquinoline, which is well known as AW/EP additive [5, 6], onto pure copper in an noble gas atmosphere was researched. Special equipment was used in order to provide a clean surface for the adsorption of the additives from their solutions, because polluting the sample surface changes its properties [7].

2 SAMPLE PREPARATION:

Copper sheets of 8x12 mm were cut. These sheets were grinded with silicon carbide abrasive papers with grid sizes from 150 down to 4000 on a Struers LaboPol-4 grinding machine. Afterwards the sheets were polished on the same machine with a MD-Dac disk treated with DP-Spray P containing polycrystalline diamonds with a grain size of 1µm. After rinsing with deionised water, the sheets were transferred into the preparation chamber (5×10^{-8} mbar) of the ESCA. There carbonaceous remnants as well as oxygen and nitrogen were removed by argon ion sputtering. The purity of the copper sheets was checked by ESCA analysis prior to preparation of the additive films.

5 µmol/ml solutions of ricinoleic acid, 8-hydroxyquinoline in toluene were prepared from the substances provided by the lubricant division of AC²T Research GmbH. The solutions were transferred into the electrochemical device, which is an extension of the ESCA. It is directly flanged to the ESCA spectrometer in order to provide the possibility to exclude oxygen during the preparation of samples and transport them into the high vacuum system of the spectrometer without pollution and exposition to air.

The electrochemical setup consists of two supply reservoirs, one was used as storage for toluene for rinsing the samples and cleaning the device the second contained the solution of the adsorbates, a pressure line, which was filled with He 6.0, to provide the pressure to transport the liquids into the adsorption vessel, an adsorption vessel, where the samples were prepared, and bubblers, to release the pressure and keep air out of the system. The whole device was permanent under a slight overpressure of He in order to keep it from being polluted. Furthermore the He is used to flush the solutions in the storage supply in order to degas the solutions.

The clean copper sheets were transferred from the preparation chamber of the ESCA spectrometer directly into the adsorption vessel of the electrochemical device. There, they were dipped in 5 µmol/ml solutions of the adsorbates for 20 minutes at room temperature. Afterwards, the samples were rinsed with toluene, blown dry with He and transferred directly without exposing them to environmental conditions into the preparation chamber of the electron spectrometer.

3 MEASUREMENT:

All ESCA measurements were performed with a Vacuum Generators Microlab Mk 2 spectrometer using aluminum K α radiation. The twin-anode was operated at a power of 795 W and adjusted to yield maximum photoelectron emission from the samples. The analyser entrance aperture was set to 20 mm and the acceptance angle was 22° for recording survey spectra and 10° for recording angle resolved spectra. Survey spectra were recorded at an angle (analyser angle) of 15° between analyser and surface normal. The energy reached from 0 eV to 1400 eV binding energy. Angle resolved ESCA spectra were collected at analyser angles of 15°, 28°, 48°, 61°, 70° and 75°. Spectra of the C 1s, the O 1s and Cu 2p photoelectron peaks were recorded for the ricinoleic acid sample and the 8-hydroxyquinoline sample. Additionally the N 1s photoelectron region was recorded for the 8-hydroxyquinoline. The measurements were performed in the analysis chamber of the ESCA spectrometer, where the pressure was always below 5×10^{-10} mbar.

4 RESULTS:

The positions of the photoelectron peaks (table 1, table 2) were determined using least squares peak fitting. A combination of Gaussian- and Lorentzian peak was used for the fit.

C 1s	O 1s	N 1s	Cu _{Surf} 2p _{1/2}	Cu _{Bulk} 2p _{1/2}	Cu _{Surf} 2p _{3/2}	Cu _{Bulk} 2p _{3/2}
286	533.6	400	954.6	953.7	934.8	933.8

Table 1 shows the binding energy in eV of the photoelectron peaks of the 8-hydroxyquinoline sample. Cu_{Surf} means the copper atoms at the surface and Cu_{Bulk} the ones in the bulk.

C 1s	O 1s	Cu _{Surf} 2p _{1/2}	Cu _{Bulk} 2p _{1/2}	Cu _{Surf} 2p _{3/2}	Cu _{Bulk} 2p _{3/2}
285.7	533.4	954.4	953.9	934.5	933.9

Table 2 shows the binding energy in eV of the photoelectron peaks of the ricinoleic acid sample.

The survey spectra of 8-hydroxyquinoline and ricinoleic acid showed no signs of impurities. Only photoelectron- and auger peaks of copper, carbon, nitrogen and oxygen were found in the spectrum of 8-hydroxyquinoline (figure1). The quantification of the O 1s and the N 1s signals showed that there was an equal amount of both oxygen and nitrogen in the adsorbed film. The position of the N 1s photoelectron peak was in good agreement with the position measured for copper 8-hydroxyquinolate [5]. The C 1s peak was in the region typical for alcohols, ethers and organic compounds containing nitrogen. The binding energy found for the O 1s photoelectron signal was like that of aromatic ethers and alcohols. Both copper peaks, the 2p_{1/2} as well as the 2p_{3/2} peak, consisted of two peaks, which indicated two different chemical states of copper (figure 2). The chemical shift between the two peaks equalled the shift between pure copper and copper oxide. The peak at the

higher binding energy grew higher as the analyser angle increased suggesting, that the copper atoms, in the higher oxidation state, were at the surface. This indicated a chemical binding of 8-hydroxy-quinoline to the copper.

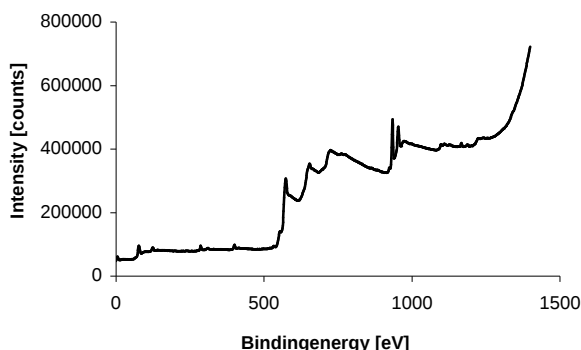


Figure 1 shows the spectrum of 8-hydroxyquinoline adsorbed onto copper.

The C 1s and the O 1s signal in the spectrum of ricinoleic acid were composed of more than one peak, which can be deduced from the shape of the signal and the shift of the maximum of the signal, indicating differently bound carbon and oxygen. The Cu 2p_{1/2} and 2p_{3/2} signal did not shift (figure 3). This was because of the much thicker film compared to the 8-hydroxyquinoline. Therefore the peak from the bulk of copper was even at 15° analyser angle too small to contribute to the signal in an amount causing a shift. The difference in the thickness of the films also influenced the background of the copper signal. The background in the Cu 2p region of the ricinoleic acid rose much steeper with respect to the signal height than the one in the Cu 2p region of the 8-hydroxyquinoline.

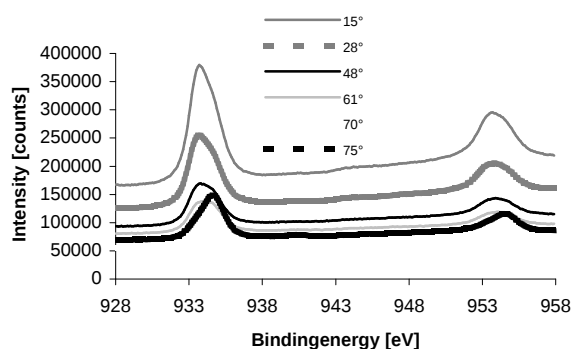


Figure 2 shows the angle resolved spectrum of the Cu 2p_{1/2} and Cu 2p_{3/2} photoelectrons of 8-hydroxyquinoline.

Quantitative information of the thickness of the films was derived using straight-line-approximation. This approximation accounted for only the electrons, which arrived at the detector without changing direction. It applied to films made of elements with low atomic mass like organic polymers or adsorbates. The intensity of a photoelectron peak was expressed as $I_{\text{Sub}} = Kx e^{-d/\lambda \cos \alpha}$, where I_{Sub} was the intensity of the substrate, K was a constant calculated from the atomic density and the

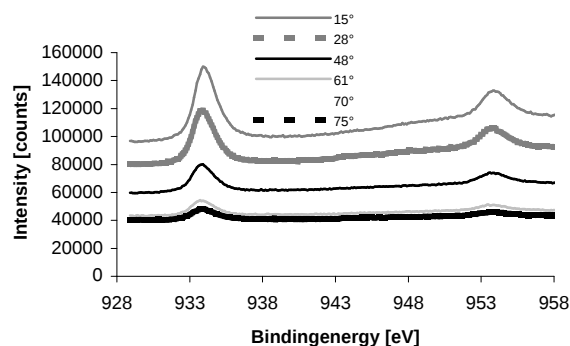


Figure 3 shows the angle resolved spectrum of the Cu 2p_{1/2} and Cu 2p_{3/2} photoelectrons of ricinoleic acid.

inelastic mean free path (IMFP), δ was the thickness of the film, λ was the IMFP and α was the analyser angle. This equation accounted for films of homogeneous thickness, which should hold for adsorbates on smooth surfaces, and an entirely covered surface. For geometric reasons the intensities of two compounds, one of the substrate the other of the film, was measured. Therefore the equation had to be modified to $I_{\text{Sub}}/I_{\text{Ad}} = K_{\text{Sub}}/K_{\text{Ad}} x e^{-d/\lambda \cos \alpha} / (1 - e^{-d/\lambda \cos \alpha})$. Considering the IMFP's to be equal the equation $I_{\text{Sub}}/I_{\text{Ad}} = K_{\text{Sub}}/K_{\text{Ad}} x (e^{d/\lambda \cos \alpha} - 1)$ was derived [8]. There the density of the ricinoleic acid was used to calculate the constants. The thickness in terms of λ was obtained from a logarithmic plot of $I_{\text{Sub}} x K_{\text{Ad}} / I_{\text{Ad}} / K_{\text{Sub}} + 1$ versus $1/\cos \alpha$ (figure 4).

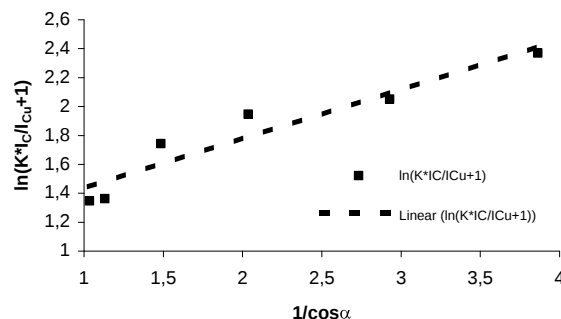


Figure 4 shows the plot of the logarithm of the ratio of the intensities of carbon and copper multiplied by a constant plus 1 versus the reciprocal cosine of the analyser angle.

λ was estimated from the formula $\lambda = 49/E^2/\rho + 0.11 x E^{0.5}/\rho$ presented by Seah and Dench [9] for calculating IMFP's for electrons, with a kinetic energy E in eV, for organic materials using their density ρ in g/cm³. The IMFP was 4.05 nm and the thickness of the ricinoleic acid film adsorbed was 1.4 nm. The thickness of the 8-hydroxyquinoline film could not be determined this way. The logarithmic plot was not the one of a line. Plotting the intensities of the two samples versus the analyser angle showed a big difference in the surface coverage (figure 5). Both samples did not cover the surface entirely, but the surface coverage of the ricinoleic acid sample is much higher. For complete surface coverage the signal of the substrate should

vanish when the analyser angle was 90°. So the model had to be modified with respect to the surface coverage. The intensity of the substrate was expressed as $I_{\text{Sub}} = Kx[(1-\theta) + \theta x e^{-d/\lambda \cos \alpha}]$ [10].

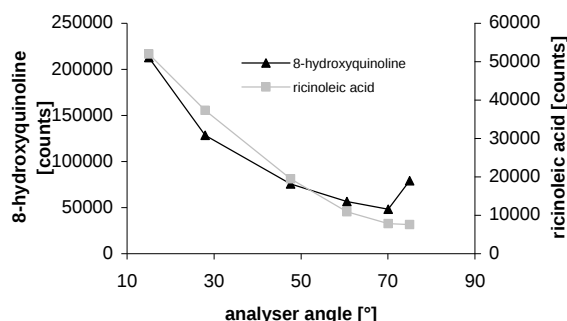


Figure 5 shows the intensity of copper photoelectrons in both samples versus the analyser angle.

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