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TRIBOCHEMISTRY OF MONOMOLECULAR LUBRICANT FILMS OF ETHANOLAMINE OLIGOMERS

A. Bogus[1], W.S.M Werner[1], I.C. Gebeshuber[1,2], N. Dörr[2] , H. Störi[1,2]

[1] Institut für Allgemeine Physik, Vienna University of Technology, Wiedner Hauptstrasse 8-10/134, 1040 Wien

[2] AC²T research GmbH (Austrian Center of Competence for Tribology), Viktor Kaplan-Strasse 2, 2700 Wiener Neustadt, Austria

ABSTRACT

The aim of this present study was to find out the influence of oxygen and nitrogen containing ethanolamine oligomers on tribological behaviour. X-ray photoelectron spectroscopy (XPS) was used to obtain insight into the molecular mechanisms leading to the macroscopic lubricity. Monomolecular lubricant films were deposited onto ultra thin copper films sputtered onto silicon wafers. Surfaces covered with the three ethanolamine oligomers were investigated by XPS before and after tribological tests, performed with the translatorily oscilating test machine and Falex micro-tribometer.

One of an unexplained mechanism are different lubrication properties of oligomers of ethanolamines. Whereas mono- and diethanolamine oligomer exhibit good lubrication properties triethanolamine oligomer do not and increase surface roughness by corrosive pit into the cooper surface.

The structure of the molecular film is elucidated using angular resolved X-ray photoelectron spectroscopy with a prototype preparation chamber, permitting the transfer of samples from liquid to the analysis chamber under Helium protective gas preventing exposure to ambient conditions. Solutions with a concentration of 250 ppm of the respective ethanolamine oligomers in double distilled water were transferred into the adsorption device, which is an extension of the spectrometer.

* Contact author: Tel.: +43-1-58801x13481
Fax.: +43-1-58801x13499
E-mail: bogus@iap.tuwien.ac.at

INTRODUCTION

Additives are of crucial importance in lubrication technology. Additive molecules physisorbed or chemisorbed onto surfaces form lubricating films fundamentally influencing wear and friction properties of two rubbing surfaces.

Earlier experiments in the macroscale as well as in the nanoscale showed that the three different oligomers of ethanolamine have different lubrication properties on 100Cr6 steel and copper [1], respectively. Ethanolamines act as multidentate ligands on the base of amino, hydroxyl and deprotonated hydroxyl groups of the total formula $NH_{3-n}R_n$ ($R = CH_2CH_2OH$, $n = 1$ to 3). Mono-, di- and triethanolamine are readily soluble in water and are utilised as additives in metalworking fluids. The understanding of the lubrication mechanisms of the additive layer chemisorbed on the specimens investigated yields important information regarding lubrication optimisation in term of the type of additive, type of isomer or oligomer and amount.

To ensure reliability of micro- and nano-devices, magnetic storage devices, the application of lubricant film is required for the protection of the sliding surfaces from wear. Ideally, these films should be in the range of monomolecular layers because of small clearances in such devices and to minimize adhesion of sliding partners and to reduce wear and friction.

The classical approach to lubrication of micro- and nano-devices uses multi-molecular layers of liquid lubricants. Boundary films are formed by

- Physisorption which no exchange of electrons takes place between the molecules of the adsorbate and adsorbent - this process involves weak van der Waals forces).
- Chemisorption which sharing of electrons and electron interchange between chemisorbed species and the solid surface by formation of covalent bonds.
- Chemical reaction where films are formed by chemical reaction of the solid surface with the environment, the additive and the solid surface.

The stability and durability of the above surface films decrease in following order: chemically reacted films (large film thickness), chemisorbed films (monomolecular layers), physisorbed films (monomolecular to multimolecular layers).

Sub-monomolecular films with a thickness in the order of few nanometers, may be discontinuous and may deposit in an island form of non uniform thickness with lateral resolution on the nanometer scale [2].

A film fully covered with one layer of additive, often referred to as a monolayer, may reduce friction, wear, and rust, or may stabilize emulsions, foams, and solid dispersions.

In this study we investigated so-called ethanolamines which have three different oligomers: monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). The chemical structures are depicted in Fig. 1. Ehanolamines are multidentate ligands through amino, hydroxyl, and deprotonated hydroxyl groups, with the total formula $NH_{3-n}R_n$(R = CH_2CH_2OH, n= 1–3).

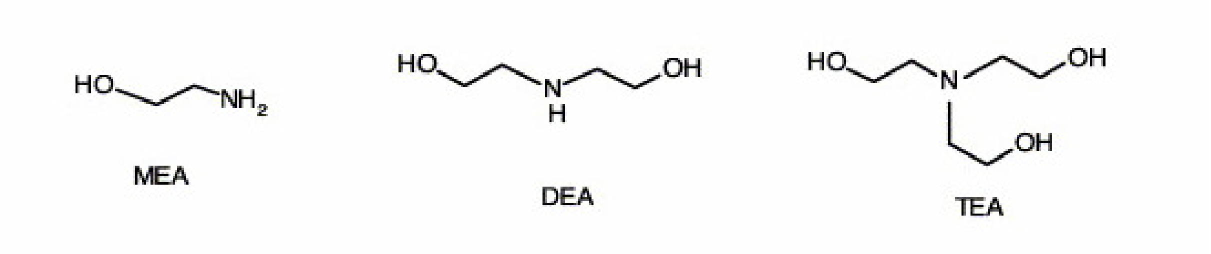

Fig.1. Three oligomers of ethanolamine [1]

Ethanolamines have a broad spectrum of applications, because they combine properties of amines and alcohols. Thus, they exhibit a unique capability of undergoing reactions common to both groups.

One not completely elucidated phenomenon concerns the different lubrication properties of oligomers of ethanolamines: Mono- and diethanolamine oligomer exhibit good lubrication properties whereas triethanolamine oligomer causes corrosive pits into the cooper surface.

In order to acquire knowledge of the tribological behavior of the oligomers at the interface between solids, a fundamental research work on the interaction of additive molecules with the surface is necessary.

XPS is the appropriate analytical method for the chemical analysis of adsorbents on surfaces. This technique is capable of characterizing the binding of the molecules to the surface as well as of providing concentration depth profiles of organic compounds adsorbed to solid surfaces. The chemical shift of the photoelectron peaks provides information about the atoms bound to the surface and is an indicator for the strength of the interaction between surface and additive. Angle resolved XPS 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. Finally, quantitative information about the composition can be gathered and quantitative concentration depth profiles are available [3].

MATERIALS AND METHODS

Sample preparation

Silicon wafers of 10x10 mm^2 were cut from 5x5cm^2 sheets, and coated with 200 nm of copper by sputtering. The surface flatness of these coated slides was determined with an atomic force microscope (AFM MFP-3D, Asylum Research Santa Barbara, CA) in contact mode in air, and it turned out that the samples were almost flat at the atomic level.

Investigations by X-ray photoelectron spectroscopy (XPS) were performed using a VG ESCALAB Mk III equipment with a prototype preparation chamber permitting the transfer of samples from liquid to the analysis chamber under Helium protective gas preventing exposure to ambient conditions. The samples were transferred from the load lock chamber into the preparation chamber (5x10^{-9} mbar) of the XPS. It is well known that polluted sample surfaces change their properties [4]. For this reason, the specimens have been cleaned by argon ion sputtering until the XPS spectra of samples showed no peaks of contamination.

100Cr6 steel samples were prepared from sheets of 8x12 mm^2, which were cut from roll from roller bearing. Then these samples were ground with abrasive paper down to 4000µm, and then with DP-Spray P containing crystalline diamond with a grain size of 1µm. The average roughnesses (RMS) of the samples were checked by AFM and gave values of approximately 20nm.

Preparation of ethanolamine oligomer solutions.

Each ethanolamine oligomer was dissolved in double distilled water to a concentration of 250ppm. All water solutions had the same molar content (molecular concentration). Concentrations of the additives were significantly below saturation concentration, to prevent growth of additive crystals on the copper surface.

For the experiments, the solutions were then transferred into the electrochemical device consisting of two supply reservoirs, one was used as storage of double distilled water for rinsing the samples and the other contained the additive solution of the absorbents. A pressure line, which was filled with He 6.0 provided the pressure to transport the liquids into the adsorption vessel. In the adsorption vessel the samples were prepared. Bubblers were used to release the pressure and to keep air out of the system. Thus, the entire device was permanent under a slight overpressure of He. Furthermore the He flow was used to flush the solutions in the storage supply in order to degas the solution [5].

The clean copper sheets were transferred from the preparation chamber of the XPS spectrometer directly into the adsorption vessel of the electrochemical device. There, they were dipped in 0.025% solutions of the adsorbates for 10 minutes at room temperature.

The clean copper sheets were transferred from the preparation chamber of the XPS directly into the adsorption vessel of the electrochemical device. There, they were dipped in 250 ppm solutions of the ethanolamines for 10 minutes at room temperature. Afterwards, the samples were rinsed with double distilled water, blown dry with He and transferred directly without exposing them to environment into the preparation chamber of the XPS [6].

Data acquisition

For XPS spectra, the samples were transferred from the preparation into the analysis chamber ($< 5 \cdot 10^{-10}$ mbar, except for sputtering). In angle resolved measurements (ARXPS), the angle between the sample surface and the analyzer, which is called emission angle, was altered by rotating the samples around the x-axis. This corresponded to rotations at angles of 0º and 80º. The emission angle was calculated from the geometric factors. Therefore, the emission angles calculated for the geometries used in the experiments were 15º and 70º.

All XPS measurements were performed using aluminum Kα radiation. The energy covered a range from 0 eV to 1400 eV binding energy. Spectra of C 1s, O 1s, N 1s and Cu 2p for silicon samples with copper layer and Fe 2p for steel samples were recorded.

Tribological experiments

The TOG tribometer, a translatorily oscillating test machine as shown in Fig. 2, was chosen for the investigation of lubricity on a macroscopic scale. TOG is widely used for the study of the tribological behavior of tribo-partners with translatory relative movement to evaluate material combinations in a dry or wet lubrication regime.

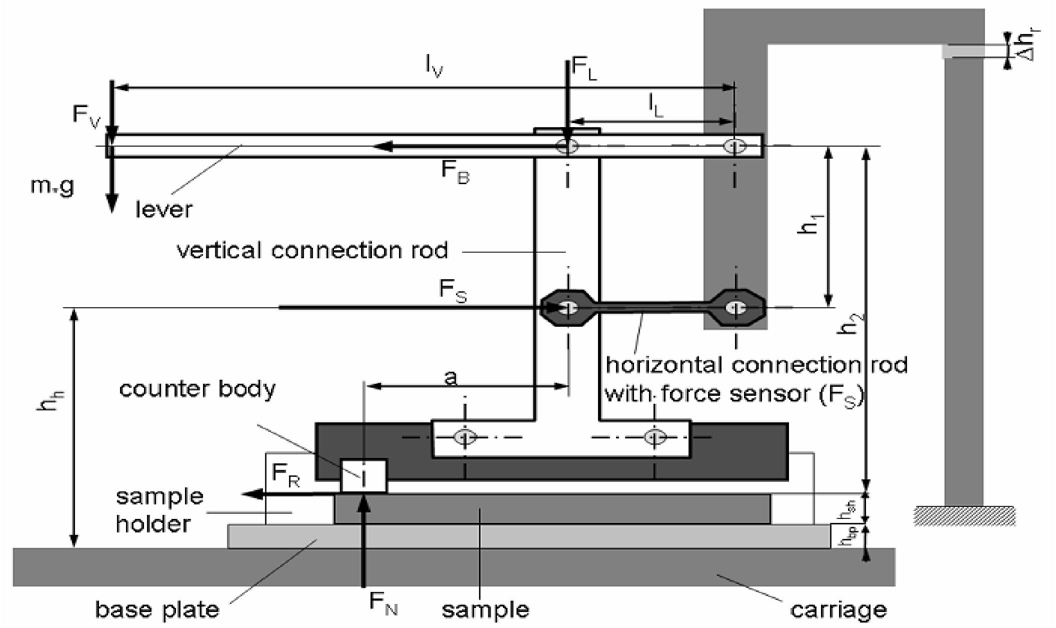

Fig.2. Sketch of the TOG tribometer with the denotation of the parts described and used for the calculation of the coefficient of friction.

The tribometer sample holder for testing in lubricants itself was screwed to a plate, which was fixed on the carriage. The carriage resides on a roller bearing and is driven by pneumatics. If the parallel lever system is adjusted in a way that the levers are parallel to the surface of the sample during tribotesting, friction force can be easily calculated from the stress measured by resistance strain gauge and the load applied and the dimensions of the tribometer.

Micro-tribometer FALEX-MUST 2D-FM

The tribometer FALEX-MUST 2D-FM working in reciprocating mode was used for copper sputtered silicon wafers to apply small loads from 1 mN to 1 N in order to prevent the silicon wafers from breaking. As counter body a steel ball mounted on a 2D force transducer was used. The normal force F_N (rectangular to the surface), the tangential force F_T (parallel to the surface of the test sample and opposing the relative velocity) and the moving way s were recorded over time t while the sample (copper coated silicon wafer) was moved in reciprocating mode.

Fig. 3 depicts the functional principle of this micro-tribometer. The FALEX-MUST 2D-FM special force transducer consists of a cantilever based on parallel spring system, two mirrors fixed on a moving part of the cantilever and a mechanical carrier. The cantilever is fixed on the mechanical carrier and helps to change the measurement mode of the force transducer. The two mirrors positioned orthogonally to each other are used as reflective surface for the fibre optic sensors (FOS). FOS is for the measurement of the deflection of the force transducer and the positioning of the piezo drives.

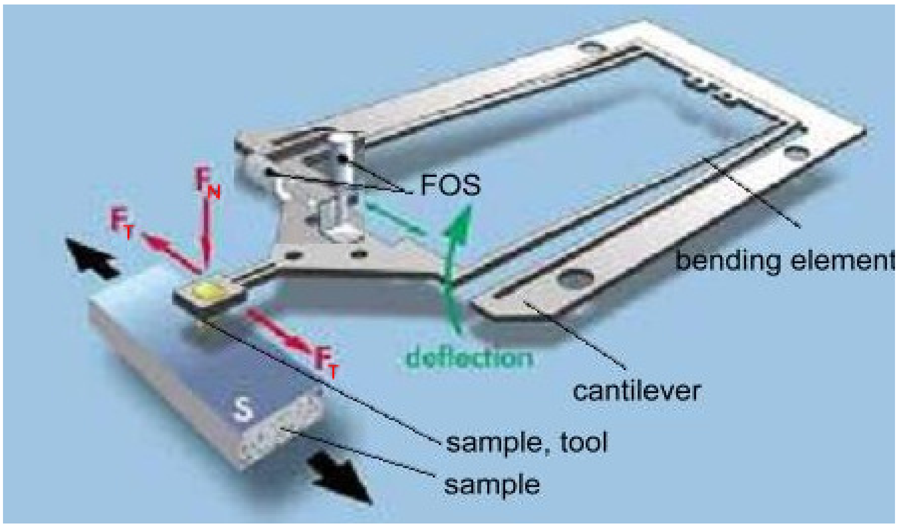

Fig. 3. Functional principle of the force transducer in microtribometer [7].

In the tribological experiments, the steel ball which was loaded against the copper coated silicon wafer. The chosen test parameters are listed in Tab. 1.

Tab. 1. Test parameters for copper coated silicon wafers sliding against steel balls in micro-tribometer FALEX-MUST 2D-FM

Material	100Cr6steel ball
Target force	30mN
Stroke length	7mm
Scan speed	5mm/s
number of cycles per track	10

RESULTS

Micro-tribometer

The results obtained with micro-tribometer show that ethanolamine oligomers dissolved in water lower the friction at a concentration of 250 ppm. Monoethanolamine oligomer reduce friction by 63% and the friction coefficient in this case is the smallest. Diethanolamine reduce friction coefficient by 25% and triethanolamine by 44% (Fig. 4).

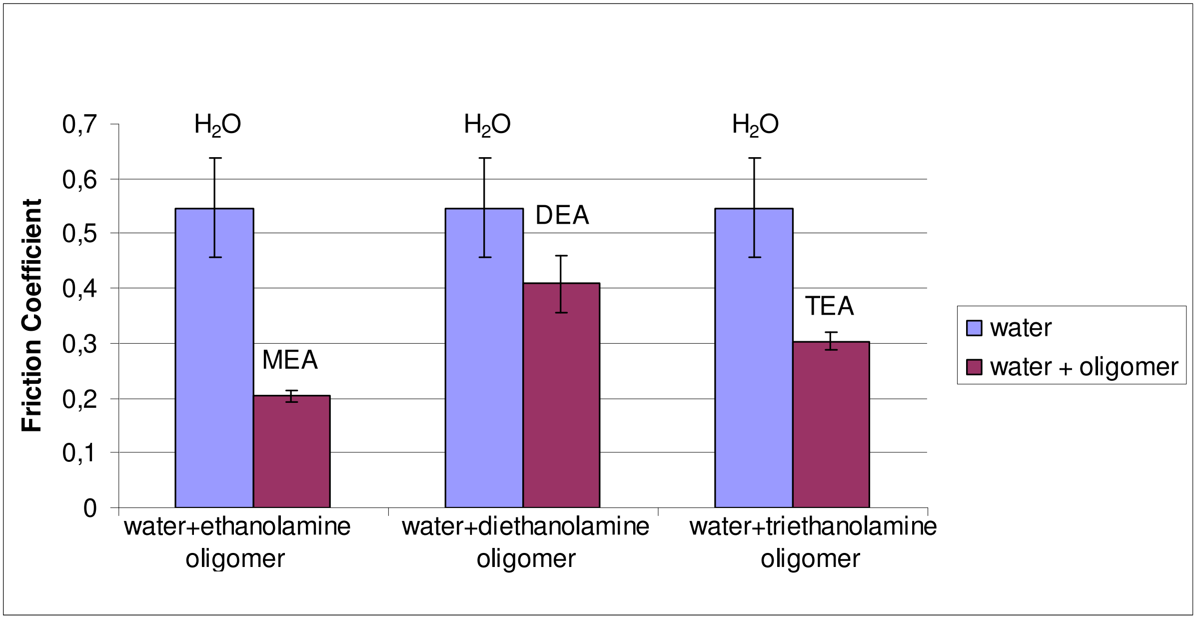

Fig. 4. Microtribometer results showing drop of friction coefficient for three oligomers of ethanolamines compare to double distilled water.

TOG

The TOG tribometer is based on a steel cylinder which is loaded against the steel sample. The sample was mounted on a special sample holder, which had been constructed for tribotesting in lubricants. During the measuring process the cylinder was oscillating in certain frequency and was in constant contact with the sample (see figure 2).

The 12N load was applied to the upper specimen holder where the cylinder was mounted to press on a sample. For substances the test were carried only once.

The results show that ethanolamine oligomers dissolved in water lower the friction at a concentration of 250 ppm. Monoethanolamine and diethanolamine oligomer reduce friction the mostly by 58% and 37%, whereas triethanolamine only by 11% .

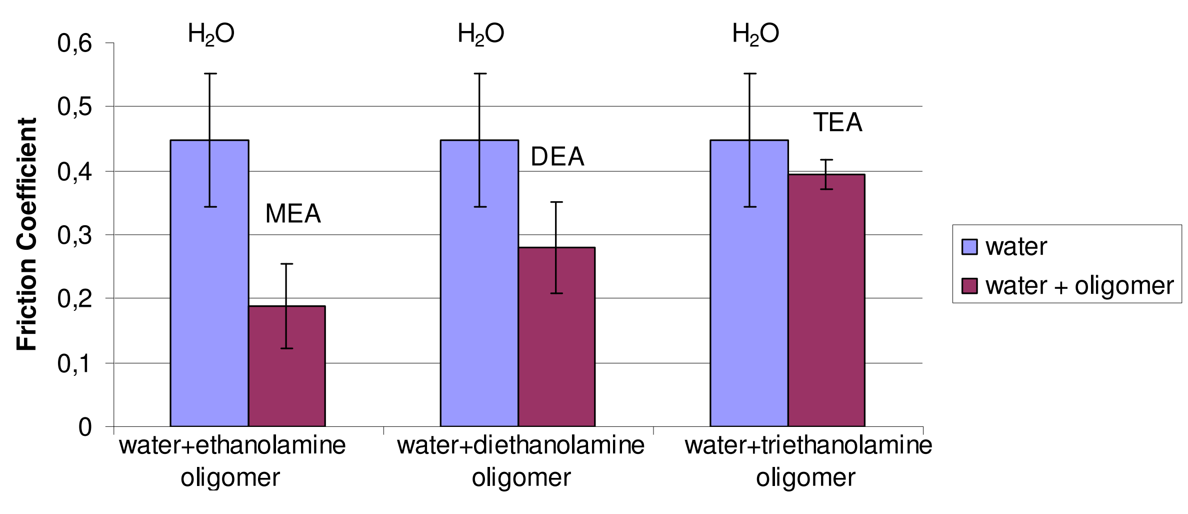

Fig. 5. TOG results showing drop of friction coefficient for three oligomers of ethanolamines compare to double distilled water.

In previous work [1] the Atomic Force microscopy investigations with nano-Newtons resolution were performed with a MFP-3D from Asylum Research. Set point - applied load on the sample by cantilever was 3.3nN. The results showed the same tribological behaviour of ethanolamines as in makroscale, that the lowest friction coefficient was observed for monoethanolamine oligomer.

The differences in tribological behaviour have been observed by AFM with 3.3 nN load, mikrotribometer with 30 mN load and with TOG tribometer with 12N load. Results show that monoethanolamine oligomer and diethanolamine oligomer have an excellent behaviour regarding all tested paramethers. Triethanolamine oligomer increases surface roughness by corrosive pit into the cooper surface.

XPS results

The survey spectra of all samples showed only peaks of copper, oxygen, nitrogen and carbon as expected. The position of photoelectron peaks was determined using Casa XPS, and a combination of Gaussian and Lorentzian peak was used for fit.

The adsorption of ethanolamine oligomers onto atomically flat surface of copper layer takes only 10 minutes. The survey spectra shows that after this time surface adsorb a measurable amount of the oligomers.

The quantification of the O1s and C1s showed that there was an equal amount of both oxygen and carbon in the adsorbed films. The C1s peak was in the region typical for alcohols and organic compounds containing nitrogen.

First results obtained for diethanolamine present clearly orientation of the molecules on the surface. Intensity of oxygen peak O1s and carbon peak C1s increase with increasing analyzer angle, and copper peak $2p_{1/2}$ and $2p_{3/2}$ and nitrogen N1s peak decreasing with emission angle (Fig. 7). This results indicates that oxygen and carbon was located on top, copper and nitrogen were beneath. Therefore it was deduced that the molecules stand upright on the surface, bound to it by the nitrogen atom. The intensity of copper continuously declines, therefore the whole surface is covered with molecules of diethanolamine.

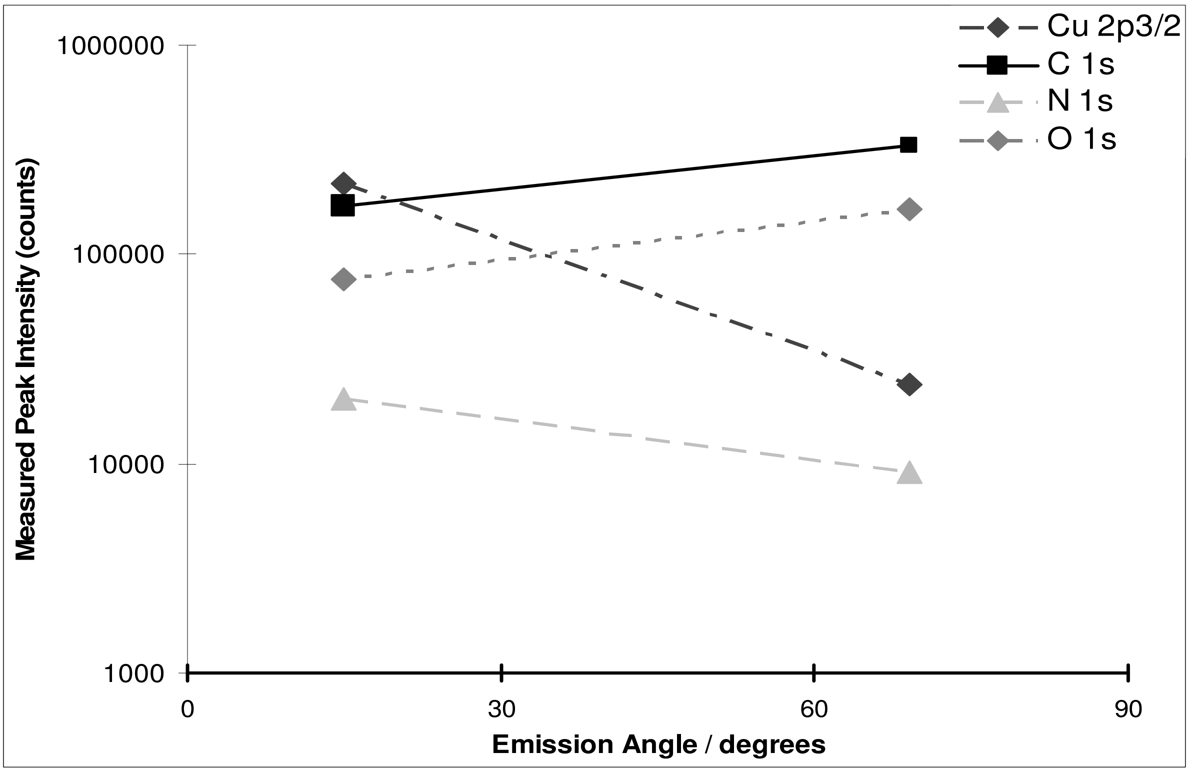

Fig. 7. Intensity ratios of diethanolamine oligomer XPS peaks depending on the take off angle (with the surface normal).

In figure 7 can be clearly see that the intensity of copper continuously declines, therefore the whole surface is covered with molecules of diethanolamine. Multi point acquisition done with Auger Electron Spectroscopy and Scanning Electron Microscopy images confirm obtained results, showed that the whole surface is covered by homogenious layer of tribofilm, and Auger spectra showed C1s, N1s and O1s peaks which are the elements of ethanolamines.

In case monoethanolamine and triethanolamine multi point acquisition done with Auger Electron Spectroscopy and Scanning Electron Microscopy image shows that not a whole surface is covered by uniform layer of ethanolamine oligomer. Auger spectra in different positions showed different amount of additives.

Additionally depth profile have been done with Ar ions in Auger Electron Spectroscopy. For three cases of ethanolamine oligomers the film created on the surface was very thin and was between 1 and 2 nm. The nitrogen, carbon and oxygen peak was observed only in the first layer (see Fig. 8) .

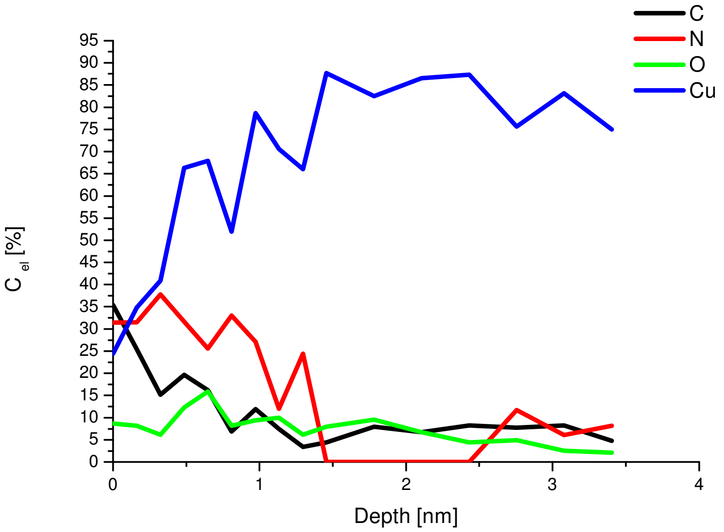

Fig. 8. Depth profile with Ar ions on AES.

Future angle resolved XPS will be done with mono and triethanolamine on copper surfaces, to prove chemical bonding between copper and nitrogen. Future studies are needed to check chemisorptions of ethanolamine oligomers on other surfaces.

DISCUSSION, CONCLUSION AND OUTLOOK

In this paper, oligomer specific lubrication has been demonstrated. The differences in tribological behavior of the oligomers of ethanolamine have been observed by AFM, microtribometer and TOG tribometer and the chemical structure of the film by XPS.

Very interesting is fact that the same behavior of friction coefficient is observed for a wide range of loads, from the nano- to the micro and macro range.

Obtained results shows that the additives undergo reactions during adsorption, and it takes only 10 minutes for the film to strongly adhere to the substrate.

The lowest friction coefficient is observed for monoethanolamine oligomer, for di and triethanolamines friction coefficient was higher. Results show that differences in tribological behavior might be caused of orientation of hydroxyl groups on the surface.

More detailed studies with all ethanolamines on steel and others surfaces shall be undertaken. Further detailed studies are necessary to link macrotribological results with information on structural chemistry obtained by XPS.

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