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Tribological properties of additives for water-based lubricants

A. Tomala[a,*], A. Karpinska[b], W.S.M. Werner[a], A. Olver[b], H. Störi[a]

[a] Institut für Angewandte Physik, Vienna University of Technology, Wiedner Hauptstr. 8-10/134, 1040 Wien, Austria
[b] Imperial College, Mechanical Engineering Department, Tribology Group, London SW7 2AZ, United Kingdom

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ABSTRACT

Fully formulated water lubricating fluids have been thoroughly described in literature. However, the influence of individual additives on tribological properties of these compositions is still not fully clear.

In this paper we present frictional, anti-wear and anti-corrosion properties for separate solutions of anti-corrosion, anti-foaming and anti-microbial agents – amines (ethanolamine oligomers, ethylamine oligomers), friction modifiers – glycols (monoethylene glycol, 1,4-butylene glycol) and amine derivatives with longer hydrocarbon chains (3-amino-1-propanol, 4-amino-1-butanol). As a reference, we also performed some tests with pure water.

The results show that the additives used in the tests in particular concentrations significantly improve tribological properties of water. The best performance – the lowest friction and no traces of corrosion – was obtained for triethylamine. Ethylene glycol and 1,4-butylene glycol significantly reduced friction, however their anti-wear behaviour was unsatisfactory. Ethanolamines, which combine properties of amines and alcohols showed an increase in friction and corrosion, but significantly reduced wear. The conclusion is that the examined additives can enhance one property of a tribosystem while adversely affecting another.

1. Introduction

Water is a low cost lubricant with a high cooling capacity but its low viscosity and corrosive properties make it unacceptable for most tribological applications. In order to adjust the performance and improve the properties of water-based lubricants, high quality additives are used, such as surface/interface active molecules [1].

The application of water base lubricants includes steady-state processes like cooling or rolling operations and non-steady-state processes like metalworking (metalforming and metalcutting mechanisms) [6]. In both cases water acts as a coolant and a lubricant, thus reducing workpiece thermal deformation, improving its surface finish, assuring longer tool life and lower friction between the tool and the workpiece, and flushing away chips from the cutting zone. Depending on the application, water base lubricants contain additives used to perform different functions: reduce tool wear, prevent corrosion and adhesion between the tool and the workpiece. The other important issue is preventing fungal and microbial growth, which can otherwise lead to health and safety hazards, filter plugging and other operational problems [2].

In general sulfur, phosphorus and nitrogen are considered as "active elements" for ferrous-based equipment, additives with these elements are investigated by many researchers to minimized friction, wear and corrosion in water lubricated systems [3]. Tokarzewski et al. synthesized phosphoryl tris(diethanolamide) DAP as a water-soluble additive, and found that the additive was suitable for non-flammable hydraulic fluid lubricants for mining and machining industry [4]. Lei et al. studied tribological behaviour of fullerene-styrene sulfonic acid copolymer as water-based lubricant additive, and found that it can improve wear resistance, load carrying capacity and anti-friction ability [5]. Kajdas in his review on additives for metalworking lubricants enumerate many corrosion inhibitors based on amines. They improve corrosion resistance and can be removed from metal parts by aqueous methods. Additionally nitrites are used to prevent anodic corrosion in electrolytic phenomena [6].

Glycols are most commonly used in hydraulic applications as friction modifiers and to stabilize concentrated fluids, preventing the separation of their components [2]. Zhang et al. investigated the friction and wear behaviours of a (Ca, Mg)-sialon/SAE 52100 steel pair under the lubrication of various polyols in water and found that the friction coefficient was much lower that of pure water [7]. Yong et al. showed a synergy between Polyethylene Glycol (PEG) and the water-soluble EP additive result in friction and wear reduction [8].

2. Aim of the paper

In this study, we are focusing on the series of additives such as ethanolamine oligomers, ethylamine oligomers and glycols. Ethanolamines combine properties of amines (amine group $-NH_2$)

* Corresponding author. Fax: +43 15880113499.
E-mail address: bogus@iap.tuwien.ac.at (A. Tomala).

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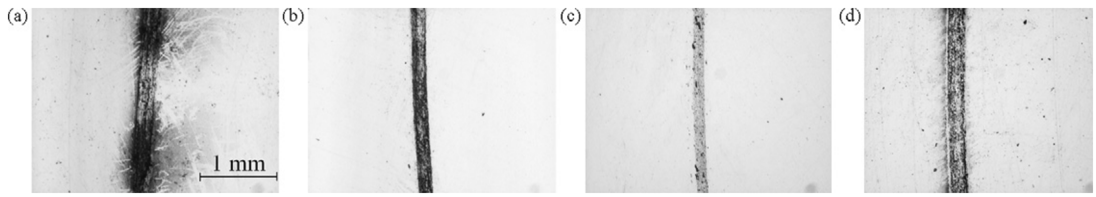

Fig. 1. Optical microscope images of disc surface after 1 h MTM test with (a) water (track width 200 μm), (b) 0.025% monoethanolamine oligomer (MEA) solution (track width 162 μm), (c) 0.05% triethylamine solution (track width 115 μm) and (d) 0.05% ethylene glycol solution (track width 176 μm).

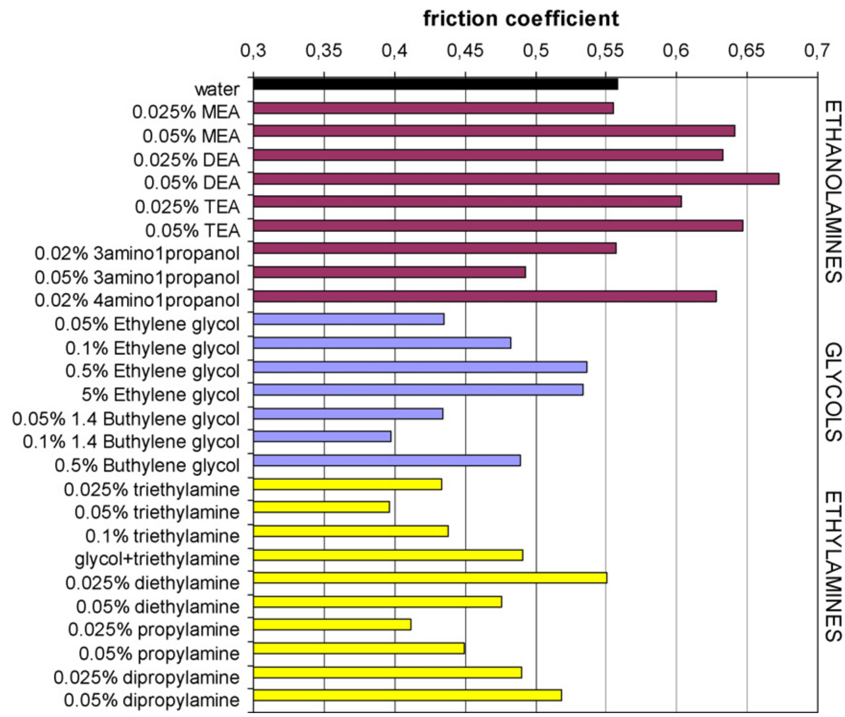

Fig. 2. Friction results for chosen additives in different concentrations.

and alcohols (hydroxyl group –OH), ethylamines contain only amine groups, glycols are the compounds having OH groups on both ends of molecule. Most of them are liquid, which makes them easy to handle, and many are soluble in water, so they are suitable for water based lubricants. They may be used as emulsifying, wetting and anti-icing agents [3]. Some of them act also as anti-microbial agents. They reduce corrosion by either forming a protective coating on the metal surface or by neutralizing corrosive contaminants in the fluid by maintaining the pH in a suitable range. They are

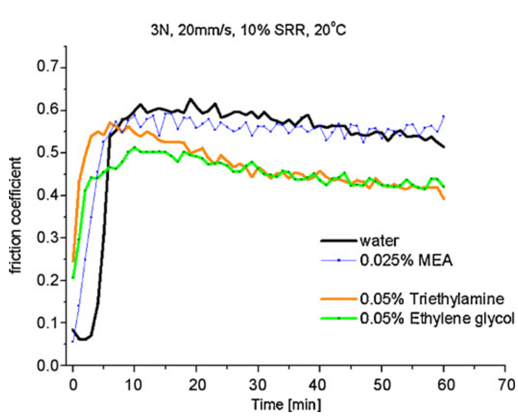

Fig. 3. Friction results for the selected additives.

employed in a wide variety of products such as hydraulic fluids and rolling oils, and very often as ingredients for cutting fluids [2].

The aim of this study was:

- To establish the mechanisms of how various individual additives influence tribological properties of the system and to select the best compounds and concentrations for this purpose.
- To clarify additives interactions with surfaces – analyze the chemical bonding and explain their effect on the tribological performance of surfaces. In particular, the effect on friction coefficient, wear mechanisms and corrosion processes in lubricated tribosystems.

3. Experiments

3.1. Materials

In this paper, we present results for separate solutions of anti-corrosion, anti-foaming and anti-microbial agents – amines (ethanolamine oligomers, ethylamine oligomers), friction modifiers – glycols (ethylene glycol, 1,4-butylene glycol) and amine derivatives with longer hydrocarbon chains (3-amino-1-propanol, 4-amino-1-butanol, diethylamine, propylamine). As a reference, we performed some tests for the same high purity water (<1 Mohm, pH 7) that was used to prepare the solutions. Water purification was done by reverse osmosis and the use of purification cartridges. To

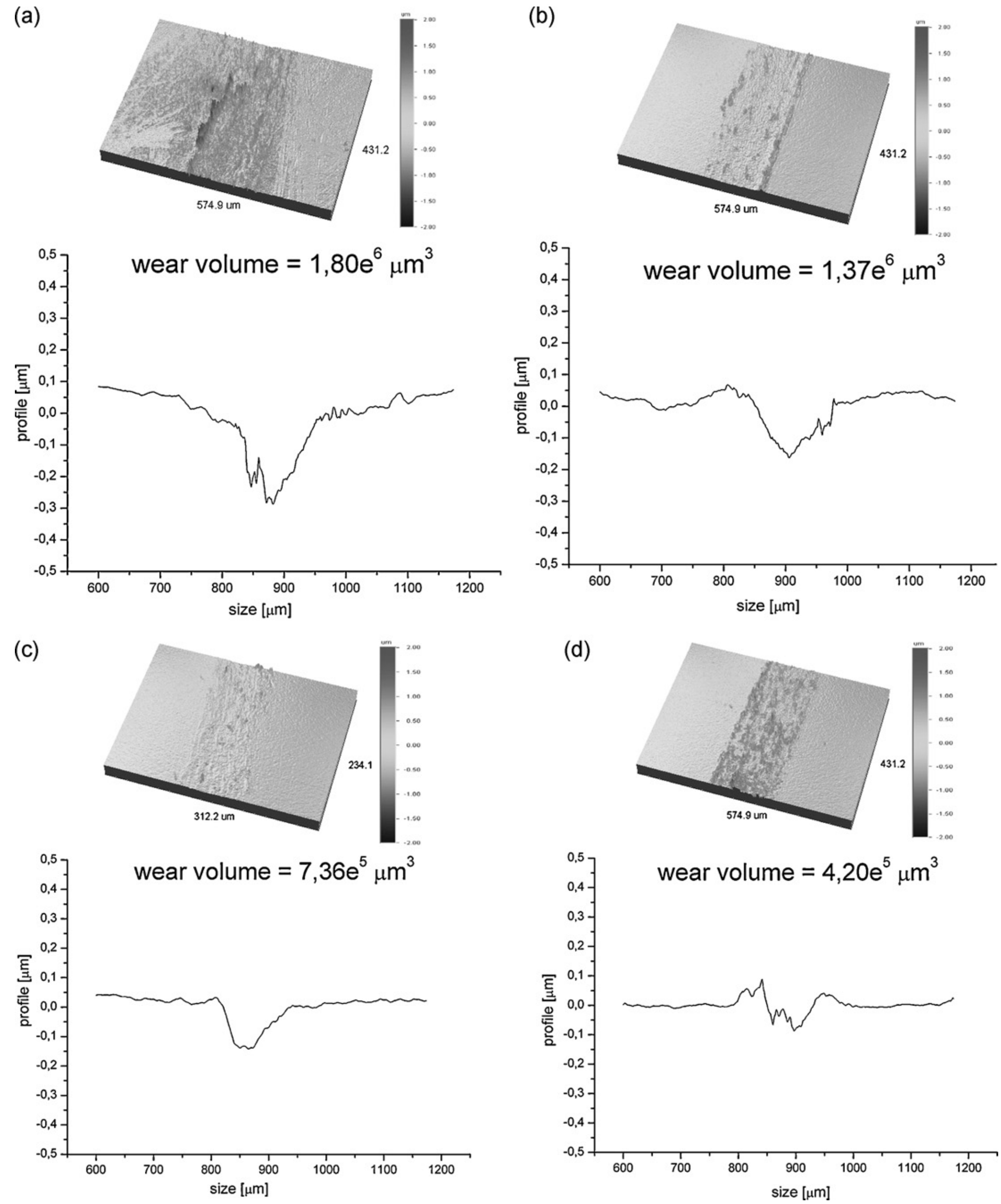

Fig. 4. 3D topography images and profiles across the wear tracks for disc specimens after MTM tests with (a) water, (b) 500 ppm ethylene glycol, (c) 500 ppm triethylamine and (d) 250 ppm MEA.

ensure the repeatability of the results, multiple tests were done for each blend.

Specimens used for tribotest were made of AISI 52100 steel (PCS instruments, London, UK). The initial disc and ball roughness was R_a = 0.01 μm, and their diameters were 46 and 19.05 mm respectively.

3.2. Test apparatus

The frictional performance of the prepared solutions was measured using a Mini-Traction Machine (MTM) to represent a mixed rolling/sliding contact between a test ball and a disc [10,11]. In this work the measurements were initially performed under 10N load (430 MPa), due to lack of reproducibility and high friction forces lower-pressure regimes (3N – 290 MPa) were selected. Ultimately, tests were performed at room temperature, under low speed (20 mm/s) and load (3N), with SRR (Slide to Roll Ratio) 10% for a period of 1 h. The test conditions were chosen in order to obtain most stable and reproducible result to enable a comparison of the additives.

Wear volume was measured using Wyko NT9100 Optical Profiler. Volume Analysis tool is included in the Vision Advanced Analysis Package, the operating software of the Wyko profiler. This method estimates the volume between the worn surface and a reference plane. The reference plane was set as the average height of the unworn area outside the wear track. Volume Analysis estimates the volume occupied by the space between a surface and a plane parallel to the reference plane of the surface that intersects the maximum height of the surface. This parameter can be seen as the volume of water that the surface must hold in order to completely “submerge” it. The wear volume was calculated for the whole disc and only the area under the reference plane was considered.

In addition, corrosion traces were visually inspected using an optical microscope.

3.3. Chemical analysis

Fresh steel specimens with adsorbed additive layers were studied with Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS). This adsorption method and equipment was described in the previous work [12]. XPS is an appropriate analytical method for chemical analysis of thin (less than 10 nm) films adsorbed on a surface, configuration of the molecules and chemical bindings to the substrate.

Analysis of AR-XPS data was performed using the ARCTIC software [13] using the surrey trend plots and stratification method. Surrey Trend Plot is a usual approach to start analyzing the angle resolve XPS spectra. It allows to judge which peaks vary in a similar fashion as the sample is tilted, and therefore which species are likely to be found together in the sample. Stratification method gives possibility to plot the results in a form analogous to a chromatogram: bars indicates the average depth of each layer, while the area of each bar tells the relative quantity of each species.

4. Results

4.1. Corrosion Inspection

The results show that additives used in the tests significantly improved tribological properties of water. Water caused severe corrosive pits on the track when no additive was present, as can be seen in Fig. 1.

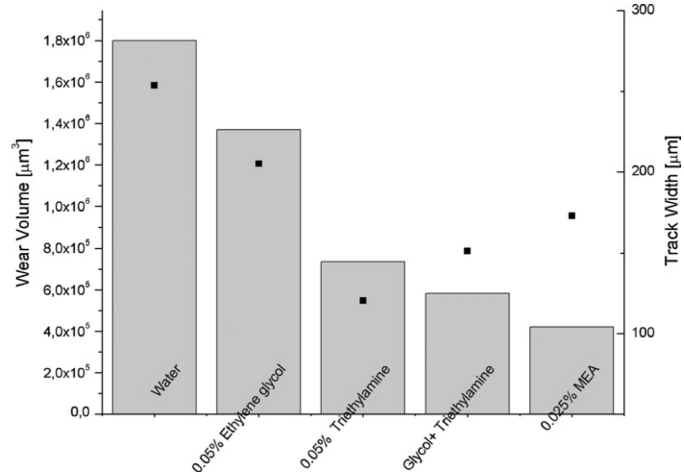

Fig. 5. Wear results for selected additive solutions and pure water. Columns show calculated wear volume, dots indicate measured wear track widths.

4.2. Frictional performance

The concentration of the additives played a very important role. The average, stabilised, coefficient of friction for each test is shown in Fig. 2.

Further results presented in this paper are for the additives representing each group (ethanolamines-monoethanolamine oligomer (MEA), glycols-ethylene glycol, ethylamines-triethylamine) in selected concentrations, which gave the best performance from each group.

The selection was carried out only for primary amines and glycols (not for derivative structures), based on friction results,

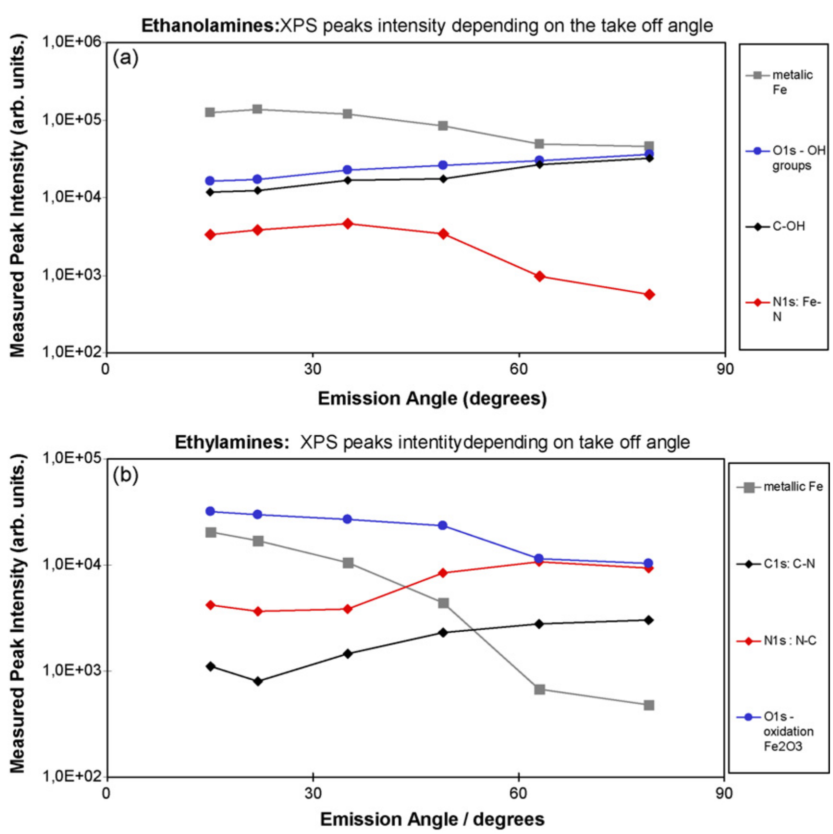

Fig. 6. (a) MEA monoethanolamine oligomer: intensity of XPS peaks depending on the take off angle (with the surface normal). (b) Triethylamine: intensity of XPS peaks depending on the take off angle (with the surface normal).

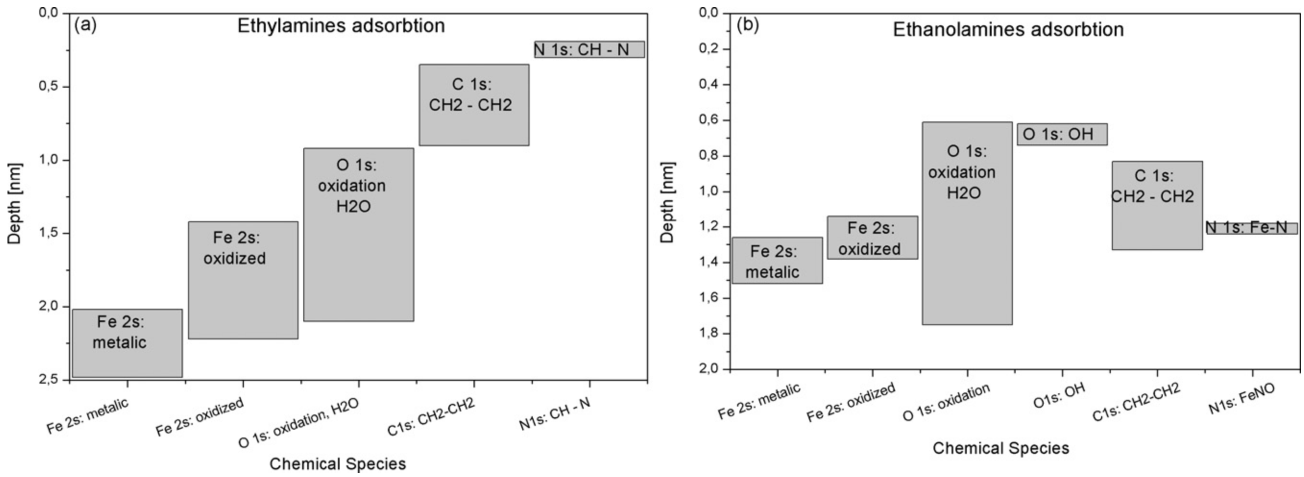

Fig. 7. Bars indicate the depth range in which the specified chemical species are present (a) ethanolamines and (b) ethylamines.

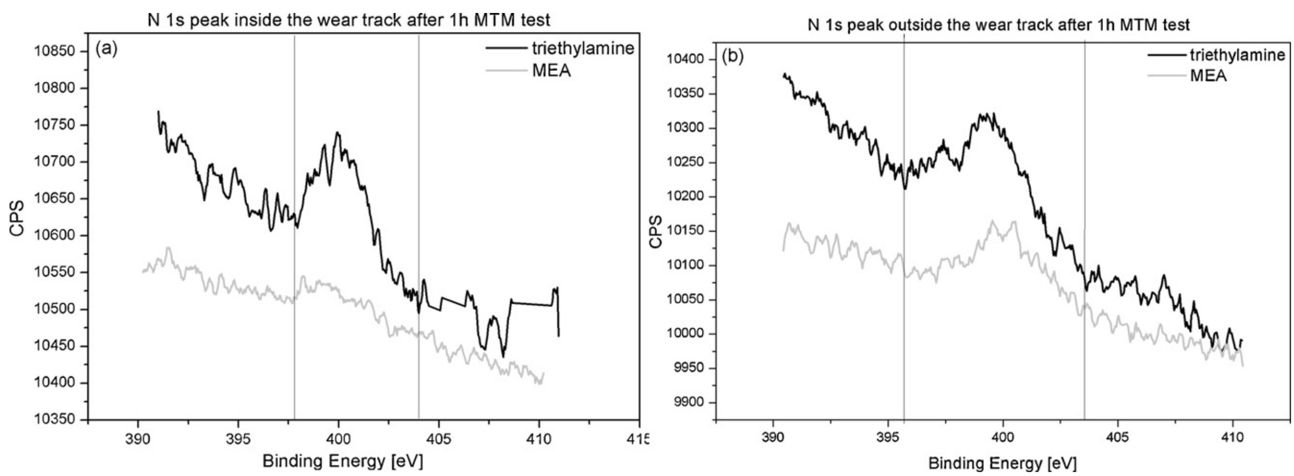

Fig. 8. N1s photoelectron peak as measured on the ball (a) inside and (b) outside the wear track for two tested additives: triethylamines – black line and monoethanolamine (MEA) – grey line.

wear measurements (track width and volume) and corrosion inspection.

Fig. 3 shows a time dependent measurement of friction coefficient for the selected additives. For triethylamine additive, at the beginning of the test friction was similar to that of pure water, but decreased with test time (after 30 min it reduced by 25%), while friction for water and MEA reminded stable.

4.3. Wear analysis

In Fig. 4 topography images of the disc wear tracks for water, glycol, triethylamine and monoethanolamine are shown. It is observed that the surface of the wear track is rough, and some corroded, plastically deformed or/and transferred material from the ball is present above the reference plane. For the wear volume calculation, only the area under the reference plane is considered.

Fig. 5 compares calculated wear volumes and measured disc wear track widths. Both Figs. 4 and 5 show that water without additives results in a high level of wear and corrosion. For ethylene glycol a considerable amount of wear and corrosion was still observed. For the additives containing amine groups (MEA and triethylamine) a significant reduction of wear was noticed, although for monoethanolamine a lot of corroded material was observed in the wear track. This fact is strictly linked with the pH of the tested solution. In case of aqueous systems, pH, concentration of oxygen and certain ions such as ammonium (NH_4^+) and hydroxyl (OH^-) ions influence corrosivity [14]. Table 1 lists the electrical conductivity and pH of the test fluids in those concentrations for which the best tribological results were obtained.

4.4. Chemical characterisation

The results of the chemical characterisation of adsorbed additives using Angular Resolved X-Ray Photoelectron Spectroscopy presented in Fig. 6a and b show that ethylamines and ethanolamines are chemisorbed on the steel surface. Behaviour of peak intensities versus take off angle demonstrates the orientation of the molecules on the surface [12].

Results obtained for ethanolamines and ethylamines present clearly the orientation of the molecules on the surface. For ethanolamines: the intensity of oxygen peak O1s and carbon peak C1s increase with increasing analyzer angle, and metallic iron peak Fe $2p_{1/2}$ and Fe $2p_{3/2}$ and nitrogen N1s peak decreasing with emis-

Table 1
Electrical conductivity and pH of the examined fluids.

	Electrical conductivity (Mohm)	pH
Water	0.9	7.0
500 ppm ethylene glycol	1.6	7.5
500 ppm triethylamine	0.7	11.3
250 ppm MEA	0.8	10.9

sion angle (Fig. 6a). This result indicates that oxygen and carbon were located on top, iron and nitrogen were beneath. Therefore it was deduced that the nitrogen atom from amine group is chemically bonded to the iron specimen, whereas OH groups comprise the top layer of the film, as shown in that Fig. 7.

Ethylamines, which are also well-known as anti-corrosion additives, adsorbed on the surface different than ethanolamines. The intensity of carbon peak C1s and nitrogen N1s peak increases with increasing analyzer angle, oxygen peak O1s and metallic iron peak Fe $2p_{1/2}$, Fe $2p_{3/2}$ decreasing with emission angle (Fig. 6b). This results indicate that Ethylamines are bonded to the iron oxide layer on the top of the steel substrate by the hydro-carbon chain, while the amine group stands on the top overlayer, as shown in Fig. 7.

An XPS chemical analysis of the wear tracks of the ball and disc specimens was conducted after the tribotests. More additive traces were detected on the ball surface, probably because the ball is subjected to more contact cycles than the disc. Additive content can be evaluated by the concentration of N1s in the spectrum, as presented in Fig. 8.

For MEA tribotests, a lot of corrosion was observed in the wear track, indicating that the additive did not fulfil its role. Chemical analysis inside the wear track showed that almost no MEA was present, whereas for a triethylamine tribotest a substantial amount of the additive was observed. Outside the wear track both additives were present in similar amounts.

5. Discussion

5.1. Ethanolamines behaviour

Ethanolamine oligomers, known for their lubricating and anti-corrosion properties [9], gave unsatisfactory results, in that the monoethanolamine oligomers did not affect the friction coefficient but the di- and triethanolamine oligomers increased it compared to pure water, as can be observed in Fig. 2. Friction reduction by 12% compare to pure water was only observed for 3-amino-1-propanol at 0.05%. It is a derivative structure from MEA with longer carbon chain. However, 4-amino-1-propanol with even longer carbon chain gave increase of friction. Generally for ethanolamine oligomers a lot of corrosion was observed in the wear track (Fig. 1). However, the wear volume in this case was very low (Fig. 5). We also consider a problem that the corrosion presented on the wear track could result in lower wear volume. Although lot of corrosion is visible with optical microscope (Fig. 1) the 3D topography image and profile are not strongly affected by corrosion (Fig. 4d). On this basis we can propose that the wear volume would not change significantly after removing corrosion from the wear track.

A characteristic advantage of ethanolamine oligomers is that they effectively protect steel surfaces from corrosion, that is why it was unexpected that for these additives the most corrosion was observed in the wear track, same as in case when both glycol and ethylamines were present in the solution. XPS chemical analysis in Fig. 8 showed that almost no additive was present on the wear track after the tribotest, while it was observed in higher concentration outside the track. On the basis of these observations, we can then propose that the additive indeed reacted with the surface but continued rolling/sliding scraped it off, leading to both wear and corrosion (tribocorrosion). A thick oxidation layer formed on the wear track, preventing ethanolamines from penetrating it. This mechanism could explain why the surface in the wear track could not be protected by the additives, whereas the clean surface outside the track stayed in perfect condition (Fig. 1). Thus, we can state that ethanolamines prevent corrosion in the absence of contact but are not good boundary lubrication additives.

5.2. Glycols behaviour

As expected, ethylene glycol significantly reduced friction (Fig. 3). Even further reduction by 30% compare to pure water was observed for 1,4-butylene glycol at 0.1%, a compound with a longer carbon chain. However, when compared to ethylamines and ethanolamines, the anti-wear and anti-corrosion behaviour of the glycols is unsatisfactory. This can be seen in Figs. 4 and 5, which compare the wear results for water, ethylene glycol, triethylamine and monoethanolamine. These observations are also in good agreement with the results reported by Singh, Wan and Igari [15–17]. They stated that the use of a lubricant containing OH groups at both ends of the lubricant molecule increases the wear of aluminium, because it forms aluminium alkoxide, thus causing a decrease in the strength of the protective oxide layer. We have demonstrated that water and glycols have poor tribocorrosion characteristics and that the wear volume is high. We neglect the fact that corrosion may reduce the wear volume because it is higher compare to ethylamines and ethanolamines in any respect.

5.3. Ethylamines behaviour

Ethylamines gave the best overall performance, a very good corrosion protection inside and outside the wear track (Fig. 1), a low friction coefficient (Figs. 2 and 3) and a low wear volume (Figs. 4 and 5). Fig. 3 shows that triethylamine reduced friction coefficient with progressing test time by 30% compare to pure water. The improved performance may be due to a better activation under rolling–sliding contact or to the formation of a more mechanically durable film. Both would be consistent with the thicker molecular film evident in the XPS results (Fig. 7).

5.4. Additive mixture

The mixture of 1,4-butylene glycol (hydroxyl group alone) and triethylamine (amine group alone) increased friction and corrosion, while the wear rate reminded lower compared to both additives tested separately (Fig. 5). The mixture showed similar behaviour to that of an ethanolamine solution (it combines properties of both amines and alcohols). Thus, mixing the additives, which separately gave very good friction results, did not give a better outcome.

6. Conclusions

Various chemical compounds have been investigated as additives for water-based metalworking fluids. The results show that the additives in specific concentration significantly improved tribological properties of water. Friction coefficient was reduced by 30% for triethylamine at 0.05% and 1,4-butylene glycol at 0.1% and by 12% by 3-amino-1-propanol at 0.05% compare to pure water. This result shows that increase of a length of carbon chain in ethanolamine and glycol molecules to some extent can improve frictional behaviour.

The results suggest that in rolling/sliding contact hydroxyl groups (OH) present at both ends of the additive molecules (glycols) increase corrosion and wear rate of the steel specimens, while amine groups on their own (ethylamines) significantly improve tribological performance. Amine and hydroxyl groups presented together in a lubricant molecule (ethanolamines and additive mixture) reduced the wear rate, but corrosion within the wear scar remained substantial.

The more general conclusion is that the additives in a mixture can enhance one property while adversely affecting another. Furthermore, the presence of an amine group in additive molecules can have a big impact on a water lubricated tribosystem.

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