Available online at www.sciencedirect.com

ScienceDirect

Procedia CIRP 13 (2014) 108 – 113

www.elsevier.com/locate/procedia

2nd CIRP Conference on Surface Integrity (CSI)

Influence of Additives in Metalworking Fluids on the Wear Resistance of Steels

A. G. Huesmann-Cordes[a*], D. Meyer[a], E. Brinksmeier[a], J. Schulz[b]

[a] *Foundation Institute of Materials Science, Division Manufacturing Technologies, Badgasteiner Straße 3, 28359 Bremen, Germany*
[b] *Wisura GmbH, Am Gaswerk 2, 28197 Bremen, Germany*
* Corresponding author Tel.: +49 (0)421 218 51185; fax: +49 (0)421 218 51102. E-mail address: huesmann@iwt-bremen.de.

Abstract

The ability of metalworking fluids (MWF) to cool and lubricate the contact zone between tool and workpiece is strongly dependent on the surface-active substances such as extreme pressure additives (EP) and passive extreme pressure additive (PEP) as well as the chemical surface properties of steel. Low alloyed steels and stainless steels were examined with a wear resistance test by applying MWF with defined varied concentrations of additives featuring different properties e.g. regarding activity and molecular structure. The wear resistance was assessed and correlated with the chemical properties of the metals. Synergistic and antagonistic effects were obtained and will be discussed. The results gained from the experiments, clearly indicate, why the amount of the additives is less decisive for wear resistance than the relative ratio of polar and unpolar EP/PEP-additives. The optimal result furthermore depends on the chemical properties of the considered surfaces.

Selection and peer-review under responsibility of The International Scientific Committee of the “2nd Conference on Surface Integrity” in the person of the Conference Chair Prof Dragos Axinte dragos.axinte@nottingham.ac.uk

Keywords: Surface Integrity; Wear; Lubrication; Tribology

1. Introduction

The important role of metalworking fluids (MWFs) in manufacturing processes like forming or machining is well described in many publications [1-5]. Besides chip removal and cooling of workpiece and tool, they reduce the friction and interact with the workpiece surface.

The surface integrity of a surface is influenced by the manufacturing process itself as well as by the used MWF and has a significant influence on the functionality of the components in subsequent applications [6]. In the year 2008 a CIRP collaborative working group (“Surface Integrity and Functional Performance of Components”) investigated the interrelationships between machining processes and the resulting surface properties by a Round Robin test. In the test, only a small amount of properties could be considered: the depth profiles of hardness, the roughness, the residual stresses and the wear resistance [7,8]. The investigated workpiece material was identical so that the varied parameter was the manufacturing process which was chosen by the participant aiming at a well-defined target of surface properties. The analysis of the wear resistance was performed by a ball grinding test which means for this case that the investigation focused on the wear behavior and its dependency from the surface properties of the machined surface. In the Round Robin test, the MWF of the wear resistance test was held constant as the main focus was the effect of varied surface integrity. This paper addresses the qualification of the effect of varied MWF compositions.

1.1. Metalworking fluids with sulfur containing additives

The common oil-based MWFs are composed of several additives in base oil like naphthenic which are meant to carry certain functions such as tool wear protection or enhanced chip formation. Additives like extreme pressure additives (EP) and passive extreme pressure additives (PEP) are commonly used as sulfur/sulfonate compounds.

The extreme pressure additives (EP), for example polysulfides, serve as carriers of inactive and active

Selection and peer-review under responsibility of The International Scientific Committee of the “2nd Conference on Surface Integrity” in the person of the Conference Chair Prof Dragos Axinte dragos.axinte@nottingham.ac.uk
doi:10.1016/j.procir.2014.04.019

sulfur. The classification is based on the chemical reactivity of the sulfur compound with non-ferrous metal. Sulfides (-C-S-C-), disulfides (-C-S-S-C-) and trisulfides are defined as inactive sulfur carriers based on their behavior in special reaction tests [9]. However, polysulfides with more than three sulfur atoms in a sulfur chain (e.g. -C-S-S-S-S-S-C-) are active sulfur carriers and able to react faster but during the wear resistant test (and machining processes) the time is not sufficient for the formation of ironsulfide, FeS [10]. Reaction-layers with sulfur compounds were obtained for example by Forbes et al. but in their investigations the sulfur compounds have a reaction time slot of several hours [11].

In this work, polysulfides with three and five sulfur atoms were examined to analyze the wear resistance of two different workpiece materials.

The passive extreme pressure additives (PEP) are overbased sodium- and calciumsulfonates which consist of a saponified alkylated sulfonacid with a high amount of the corresponding carbonate- so called solid lubricants. Ciza describes the structure of the sulfonate/carbonate complex as a micelle in which the carbonate is surrounded by the sulfonate [12] but the real structure is not known.

The effect of sulfur in MWF is discussed by several references. Rehbinder e.g. describes the diffusion of surface active compounds into micro cracks at the metal surface of the workpiece [13]. Until now, the working mechanisms of these additives and their favourable influence on the surface integrity and functional performance are not completely determined [10, 14-15].

Consequently, the purpose of this paper is the investigation of the wear behavior of materials like 100Cr6 (AISI 52100), a high carbon, chromium low alloy bearing steel, and X8CrNiS18-9 (AISI 303), a high chromium, nickel containing austenitic stainless steel. The types of sulfur additives and their concentration in the MWF were varied to reveal the effects of different (active and non-active) sulfur additives on the surface chemistry after the wear resistance test and can be explained by the theory of adsorption [10]. To avoid interference by undesired effects as they occur in complex manufacturing operations, a simplified tribological test was carried out.

2. Experimental Setup

2.1. The wear resistance test

The wear resistance tests under different lubrication conditions were carried out with an apparatus according to Brugger applying standardized conditions from DIN 51347 (table 1).

A rotating friction ring (60 HRC hardened steel, X210CrW12 (AISI D6)) produces wear areas at the lateral surface of the fixed test cylinder (see figure 1), which was poured over with 8 ml MWF before starting the test. The time of load with MWF amounts 30 seconds. Then the main axes of the ellipse shaped scars (worn areas) were measured.

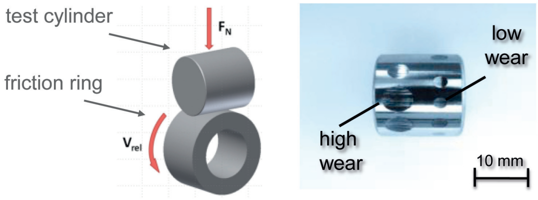

Fig. 1. Schematic illustration of the tribological test and a machined test cylinder.

Tab. 1. Conditions of the wear resistance test.

Conditions	
test cylinder Ø = 18 mm, h = 18mm	stainless steel **X8CrNiS18-9** (AISI 303), Ra = 0.78 +/- 0.13 µm, Rz = 6.05 +/- 1.26 µm rolling bearing steel **100Cr6** (AISI 52100), Ra = 0.07 +/- 0.01 µm, Rz = 0.74 +/- 0.08 µm
friction ring Ø = 25 mm, h = 12mm	hardened steel, **X210CrW12** (AISI D6) 60 HRC Ra = 0.81 +/- 0.14 µm Rz = 5.92 +/- 0.74 µm
test load/time	400 N / 30 s
rel. speed	75 m/min

The result is documented as the worn surface area by calculating the area of an ellipse in mm^2. A small value indicates low wear and indicates that the MWF has a favourable influence on the surface integrity of the material. The friction ring was ground manually after each test applying a grinding rod (grain size 120) and a standard protocol. Generally, a new friction ring has to be applied as soon as a diameter of less than 24.5 mm is achieved. The method showed a good reproducibility of the results and the deviations of measured values were within ±10% (triple determination of all examined conditions). The same steel batch was used for the production of the respective test cylinders and friction ring to allow for a reliable comparability.

2.2. Additives in MWF

The examinations were carried out with solutions containing different types of sulfur-containing additives (see Fig. 2): polysulfides (PS) and overbased sodiumsulfonate (OBS).

The polysulfides vary in the relative amount of sulfur, activity, and the space required by the side chains. PS 20 is an inactive sulfur species with a sulfur content of approximately 21.5%w and three sulfur atoms in the linear chain. PS 32 has an active sulfur content of

30.5%w and five sulfur atoms in the linear alkyl chain This molecule is more active than the PS 20. PS 40 is also an active polysulfide with five sulfur atoms in the chain but the alkyl chains are branched and bulky. The sulfur content amounts 40.0%w [10].

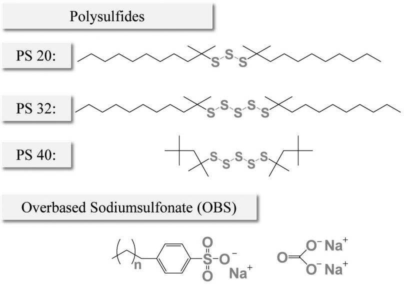

Fig. 2. Molecular structure of the EP/PEP-Additives.

The overbased sodiumsulfonate (OBS) has a sodium content of 18%w and consists of a sodium saponify alkylated sulfonacid with a high amount of the corresponding sodium carbonate [12].

3. Results and Discussion

3.1. MWF raw materials

In a first approach, the undiluted chemical substances shown in figure 2 were examined regarding their ability to reduce wear of 100Cr6 test cylinders.

In figure 3, the results of the test are shown. In comparison to the naphthenic base-oil, the value of the polysulfides and the overbased sodiumsulfonate are decreased. Regarding the polysulfides, the size of the worn area unexpectedly increases with increasing sulfur content and with the “activity” of the polysulfides. This effect can be explained by the higher complexity of the molecular structure. Another important aspect is the superior lubricating ability of overbased sulfonates compared to the polysulfides.

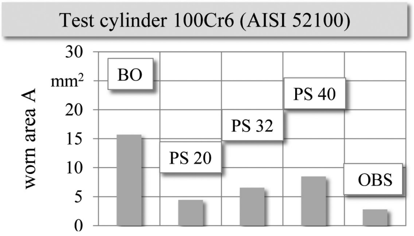

Fig. 3. Worn area of the undiluted raw materials: base oil (BO), polysulfides (PS) and overbased sodiumsulfonate (OBS).

These findings have shown that there is a considerable influence of varied additives on the wear resistance in direct contact between two metal surfaces (friction ring and test cylinder). However, it has to be considered that the additives were used undiluted, which does not reflect real working conditions.

3.2. Influence of varied additive combinations on wear

In the next investigations, the MWF consisted PS (PS 20 or PS 40) and OBS both diluted in base oil with varied concentration ratios. As, independently from the type of sulfur containing additive, the amount of elementary sulfur is discussed to be the decisive factor for the interactions between MWF and surface [10, 16, 17, 18], the polysulfide concentration of the respective tested solutions was adjusted to 10%w sulfur to made sure that the expected results of the wear resistance test can be compared.

In figure 4, the results of the wear resistance test for the mixture of PS 20 and PS 40 with varied OBS-concentration on 100Cr6 test cylinder are shown. The worn area decreased with increasing OBS when using PS 40. However, no effect was obtained for PS 20. Furthermore, the wear resistance of 100Cr6 is generally improved if the MWF contains PS 20 instead of PS 40.

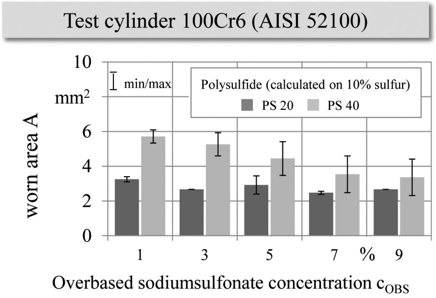

Fig. 4. Comparison of the worn areas when using PS 20 and PS 40 with varied OBS-concentration in BO on 100Cr6 test cylinder.

Even when assuming that the sulfur of the PS in the solutions interacts with the iron atoms at the surface of the 100Cr6 test cylinders by a chemical reaction, the activated PS 40 would react faster than PS 20 and show a better wear resistance because of the higher “activity”. The results show in contrast that the PS 20 solutions led to smaller worn areas. This can be explained by reversible interactions like physical adsorption (Van der Waals forces and in special limited hydrogen bridge bonds) [10]. The smaller worn area at the metal surface with PS 20 consequently is the result of the available amount of molecules which are able to interact with the metal surface. In this case, due to the molecular weight in comparison with the number of sulfur atoms in the sulfur chain of the additives, more PS 20 molecules than PS 40 molecules were present in the solution.

Obviously, the surface of the 100Cr6 test cylinder can be better protected by the higher amount of PS 20 molecules compared to the amount of PS 40 molecules at the surface during the wear resistance test.

3.3. Influence of the workpiece material 100Cr6 and stainless steel on the wear progress

The results have shown that wear can be specifically reduced by increasing the amount of OBS in combination with PS 40 but this finding does not apply to all steels. Therefore, in the next step a different metal alloy was additionally examined: stainless steel X8CrNiS18-9. The two materials differ in the composition, structure, and very important: the chemical surface properties. Bhargava et al. have shown by X-ray photoelectron spectroscopy (XPS) that at the surface of iron samples (99,95 % purity) iron oxides and iron hydroxides were located [19]. In contrast, the stainless steel (X8CrNiS18-9) features solely oxides especially chromium oxides and iron oxides at the surface [20].

The two materials were investigated in the tribology test apparatus by applying MWF consisting 5%w, 15%w or 25%w PS 40 in combination with increasing OBS content of 1%w, 5%w or 9%w solved in base oil. The results in terms of worn areas are shown in figure 5.

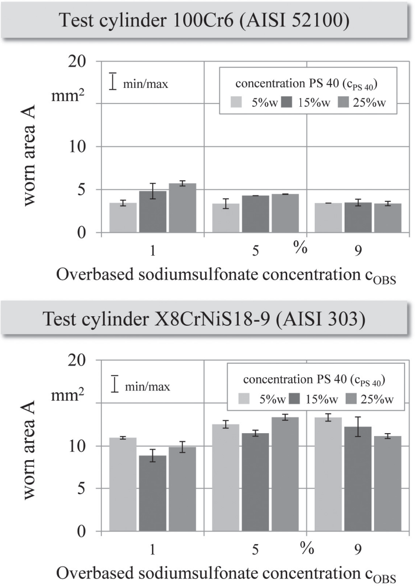

Fig. 5. Comparison of varied PS 40 with varied OBS-concentration on two different materials: 100Cr6 and X8CrNiS18-9 test cylinder.

In general, the resulting worn areas of the X8CrNiS18-9 surface are higher than at the surface of 100Cr6. The results of the stainless steel show that at a constant PS 40 concentration the size of the worn area increases with rising OBS content. With rising PS 40 concentration the size of the worn area decreases slightly at constant OBS concentration. It is clear to see that the OBS has no significant influence on the wear resistance of the stainless steel surface.

On the 100Cr6 test cylinder, the size of the worn areas by using the same solutions decreases with rising OBS concentration at constant PS 40 concentration. In contrast, the size of the worn area increases with rising PS 40 concentration at constant OBS concentration. At high OBS concentrations (9%w), the wear remains at a constant low level despite rising PS 40 concentration. The wear also constantly remains at a low level if the mixture contains only 5% PS 40 and the OBS concentration increases. These results might appear unexpected but are compatible with the theory of reversible working mechanism by adsorption [10].

OBS is a substance with an ionic character [14] so that the ionic groups are able to interact with the polarized iron at the hydroxides, for example at the surface of 100Cr6. Compared to 100Cr6, the OBS is not able to interact with stainless steel (X8CrNiS18-9) because the surface is covered with iron oxides and a thin layer of chromium oxide. The working mechanism is illustrated in figure 6. The nonionic polysulfides can interact with the iron of the oxides and also limited with the hydroxides at the metal surface but in this case by hydrogen bridge bonds.

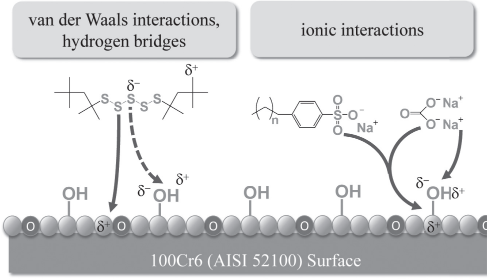

Fig. 6. Assumed working mechanisms of polysulfides (EP-additives) and overbased sodiumsulfonate (PEP-additives) to reduce wear.

The consideration of these working mechanisms of the additives enables the explanation of the presented findings. For stainless steel, the OBS have no positive influence on the wear resistance because it could not interact with the surface covered by oxide groups. In addition, it is possible that the OBS prevents the attachment of PS 40 to the metal surface, which would explain the slight increase of the worn area in figure 5 at constant concentration of PS and increasing concentration of OBS (antagonistic effect). However, the nonionic PS 40 is able to interact with the positive polarized iron-atoms of the iron oxides at the surface and influences the ability to prevent wear positively.

The 100Cr6 surface carries iron oxides and iron hydroxides which means that in this case, the additives compete on available docking sites. The derived explanation for the mechanism of MWF with a constant concentration of 1%w OBS and increasing PS 40 concentration is outlined in figure 7.

● PS 40	-	5 %w	15 %w	25 %w	25 %w
● OBS	1 %w	1 %w	1 %w	1 %w	-
worn area	9.1 mm^2	3.4 mm^2	4.8 mm^2	5.7 mm^2	7.0 mm^2

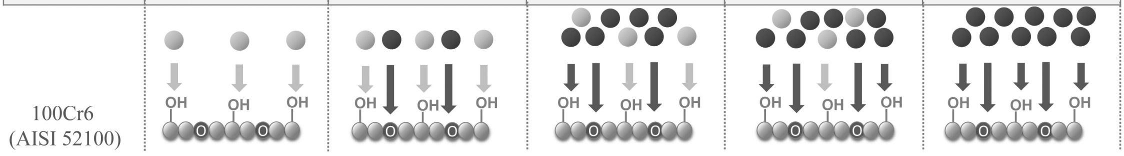

Fig. 7. Shematic illustration of the assumed working mechanisms of EP/PEP-Additives to reduce wear depending on the ratio of PS to OBS on 100Cr6. PS 40 can interact with the iron of the oxides and also with the hydroxides (limited). The OBS can interact only with the polarized iron of the hydroxides.

The presence and the relative ratio between hydroxides and oxides at the metal surface depends on several parameters, for example temperature, humidity, mechanical loads and effects of pre-machining. These effects cannot precisely be anticipated for the wear resistance test. Consequently, the investigations were carried out with the same parameters so that they did not have an influence on the comparability of the results.

In figure 7, the precise ratio of the functional groups at the surface represents an assumption. As the relative ratio changes to higher PS 40 concentration, the number of OBS molecules, which get the opportunity to interact with the hydroxide groups at the surface, decreases. Possibly, the PS 40 molecules can also interact with the hydroxide groups but the hydrogen bridge bonds and/or van der Waals forces are weaker compared to the ionic interactions. So the wear increases with increasing number of PS 40 molecules in the solution caused by the antagonistic effect in connection with the hydroxide group.

If the MWF is free of PS, the worn area increases again. On the other hand, the application of MWF without OBS also results in an inferior lubrication. The isolated additives lead to inferior wear resistance compared to the mixture. The decisive factor for the technical performance of the MWF is the ratio of the two types of additives. There is an optimum regarding the combination of EP/PEP-additives. Interestingly, this optimum is again strongly dependent on the molecular structure of the additives and in this context the space required by the PS molecules depending on the size and structure of the side chains.

Finally, the optimum of both compounds is described by a synergistic effect because both additives have the possibility to interact with their suitable groups side by side.

3.4. Influence of different polysulfides on the wear resistance of 100Cr6.

The investigations have shown that the wear resistance can be influenced by the concentration ratio of PS to OBS depending on the material and that the interactions between the metal surface and MWF can be traced back to adsorption layers.

To get an idea about the molecular processes at the surface, it should be clarified, whether polysulfides with different side chains and corresponding molecule size have a specific influence on the wear resistance.

Figure 8 presents the received sizes of worn areas obtained from three differently sized polysulfides with constant OBS (5%w) at a 100Cr6 surface. In this case, the amount of polysulfide in the solution was adjusted to the amount of substance in mmol PS relating to 100g MWF. This allows a better comparability. With increasing complexity of the molecules of the polysulfides (PS 20 < PS 32 < PS 40), the optimal ratio between OBS and polysulfides can be found at a lower relative concentration of the polysulfide.

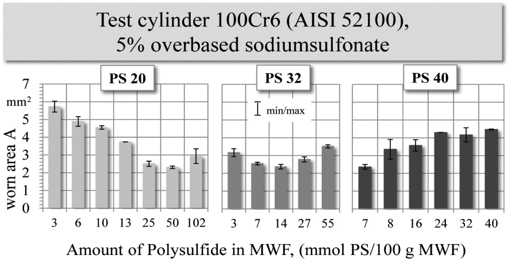

Fig. 8. Influence of the different polysulfides on the wear.

This is a steric effect as for the smallest PS 20 molecule, the addition of more molecules leads to the interaction of more additive molecules with the surface. For the more complex molecules like PS 32 and PS 40, the optimum ratio is achieved at lower relative concentrations of the polysulfide because the docking sites for the OBS at the metal surface are blocked earlier by a lower number of PS molecules. One PS 40 molecule blocks a larger area and thus more docking sites at the metal surface than a PS 20 molecule during the adsorption. So, also the structure of the side chains of the polysulfides has an important influence on the wear resistance test and consequently also on the surface integrity.

4. Conclusion

This paper shows that the wear resistance of a surface is not only determined by the manufacturing process but also by the chemical properties of the material and the used MWF. The general chemical conditions have a significant influence on the machining processes as well as on the functional performance of parts during their service life.

The presented results have shown that the EP and PEP additives have a favourable influence on the wear resistance, which is strongly dependent on the chemical properties of the metal surface and their interactions with each other. Based on considerations regarding the time in the test [10], it has to be assumed that the nascent metal surface generated during the test (material is removed) is covered immediately by oxides and hydroxides. The combination and the concentration of the different sulfur additives have a significant influence and can be explained by the formation of hydrogen bridge bonds and van der Waals forces between the polysulfide, overbased sodiumsulfonate, and the functional groups of the metal surface.

MWFs which work fine for 100Cr6 (AISI 52100) might not work for a stainless steel because the ionic additive molecules are not able to interact with the oxides of the steel surface. Depending on low alloyed steels, the investigations have shown that the wear resistance can be controlled by the concentration ratio of PS to OBS. An optimal ratio was found for PS 40, PS 32 and PS 20. For the given circumstances, the optimal combinations of the PS and OBS is depending on the specific molecular structure of the side chains of the examined additives. Looking at stainless steel, OBS has no positive impact on the wear resistance contrary to PS.

The EP and PEP-additives are only two species of additives which are applied in commercial MWF. It is very important to carry out further investigations to understand the mechanisms of complex MWF compositions and their influence on the surface integrity and functional performance completely.

Acknowledgements

The presented work is part of the CoolArt-project, which was granted by the European Research Council (ERC). The authors acknowledge finding of this work.

References

[1] Diekhoff, W., 1988. Kühlschmierstoffe für die Metallbearbeitung, Werkstatt in der industriellen Fertigung, 78, p. 515-518.

[2] Garbrecht, M., Heinzel, C., Eckebrecht, J., Koch, T., Brinksmeier, E., 2008. Relevance of Cutting Fluids in Manufacturing Processes, Proceedings of the Lubrication Management and Technology Conference, LUBMAT, San Sebastian/Spain.

[3] Brinksmeier, E., Koch, T., Walter, A., 2008. Wie viel Schmierstoff ist nötig - effizienter Einsatz von Kühlschmierstoffen, Industrial Ecology, Vieweg und Teubner, p. 110-118.

[4] Koch, T., Brinksmeier, E., 2007. Kühlschmierstoffe als gleichrangige Systemkomponenten, Schleifen und Polieren 2, p. 78-85.

[5] Weidel, S., Engel, U., Merklein, M., 2010. Basic investigations on boundary lubrication in metal forming process by in situ observation of the real contact area, Production Engineering, 4, p. 107-114.

[6] M. Field, J.F. Kahles, 1971. Review of Surface Integrity of Machined Components, Annals of the CIRP, 20 (2), p. 153-163.

[7] E. Brinksmeier, G. Levy, D. Meyer, A.B. Spierings, 2010. Surface Integrity of Selective-laser-melted Components, Annals of the CIRP, 59 (1) p. 601–606.

[8] Jawahir, I.S., Brinksmeier, E., M'Saoubi, R., Aspinwall, D.K., Outeiro, J.C., Meyer, D., Umbrello, D., Jayal, A.D., 2011. Surface integrity in material removal processes: Recent advances, CIRP Annals- Manufacturing Technology, 60 (2) , p. 603–626.

[9] Totten, G. E., Westbrook, S., Shah, R.J., 2003. Fuels and lubricants handbook: technology, properties, performance, and testing, Band 1, ASTM International, p. 515.

[10] Schulz, J., Holweger, W. 2010. Wechselwirkung von Additiven mit Metalloberflächen, expert-Verlag.

[11] Forbes, E. S., Reid, A. J. D., 1973. Liquid phase adsorption/reaction studies of organo-sulfur compounds and their load carrying mechanism, ASLE Trans. (16) 1, p. 50-60.

[12] Cizaire, L., Martin, J. M., Le Mogne, Th., Gresser, E, 2004. Chemical analysis of overbased calcium sulfonate detergents, Coll. Surf. 238, p. 151-158.

[13] Lichtmann, W. I., Rehbinder, P. A., Karpenko, G. W., 1964. Der Einfluss grenzflächenaktiver Stoffe auf die Deformation von Metallen, Akademie-Verlag, Berlin.

[14] Koch, T., Brinksmeier, E., Meyer, D., 2012. Improvement of the Scientific Understanding of Metalworking Fluids: an Interdisciplinary Challenge, Proceedings of the 18th International Colloquium Tribology, Esslingen, 2012, (CD).

[15] Brinksmeier, E., Lucca, D. A., Walter, A., 2004. Chemical Aspects of Machining Processes, Annals of the CIRP 53, 2, p. 685-699.

[16] Batchelor, A. W., Cameron, A., Okabe, H., 1985. An Apparatus to Investigate Sulfur Reactions on Nascent Steel Surfaces, ASLE Transactions, 28,4, p. 467-474.

[17] Brinksmeier, E.; Huesmann, A.-G., Schulz, J.,2012. Mechanism of Sulfur containing Metal Working Fluids at Metal Surfaces by Scratch Experiments, LUBMAT, Bilbao/Spain.

[18] Schulz, J.; Brinksmeier, E.; Huesmann-Cordes, A.G; Gebert, K.: Interactions of additives with metal surfaces – AW-additives. GFT-conference, 30.09.-02.10.13, Göttingen, Germany.

[19] Bhargava, G., Gouzman, I., Chun, C.M., Ramanarayanan, T.A., Bernasek, S.L., 2007. Characterization of the "native" surface thin film on pure polycrystalline iron: A high resolution XPS and TEM study, Applied Surface Science, 253, 9, p. 4322-4329.

[20] Henkel, B., Henkel, G., 2001. Hinweise zum Passivschichtphänomen bei austhenitischen Edelstahllegierungen, Nr. 45/Rev. 03, Technical Bulletin, Henkel Beiz- und Poliertechnik GmbH & Co.KG, p. 1–3.