Formation of carbonaceous nano-layers under high interfacial pressures during lubrication with mineral and bio-based oils

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In order to better protect steel surfaces against wear under high loads, understanding of chemical reactions between lubricants and metal at high interfacial pressures and elevated temperatures needs to be improved. Solutions at 5 to 20 wt. % of zinc di-2-ethylhexyl dithio phosphate (ZDDP) and chlorinated paraffins (CP) in inhibited paraffinic mineral oil (IPMO) and inhibited soy bean oil (ISBO) were compared on a Twist Compression Tribotester (TCT) at 200 MPa. Microscopy of wear tracks after 10 seconds tribotesting showed much smoother surface profiles than those of unworn areas. X-ray photoelectron spectroscopy (XPS) coupled with Ar-ion sputtering demonstrated that additive solutions in ISBO formed 2–3 times thicker carbon-containing nano-layers compared to IPMO. The amounts of Cl, S or P were unexpectedly low and detectable only on the top surface with less than 5 nm penetration. CP blends in IPMO formed more inorganic chlorides than those in ISBO. It can be concluded that base oils are primarily responsible for the thickness of carbonaceous nano-layers during early stages of severe boundary lubrication, while CP or ZDDP additive contributions are important, but less significant.

Key words: lubricants, vegetable oils, tribology, X-ray photoelectron spectroscopy

INTRODUCTION

Wear and friction remain one of the most frequent technical problems in engineering. Very often tribology issues are addressed by using specialized lubricants, which are designed to operate under a specific set of conditions: velocities, loads, temperatures, surfaces, etc. Under high interfacial pressures (i. e. loads) and low velocities of lubricated surfaces, the so-called boundary lubrication takes place, which is considered one of the most problematic regimes in tribology. Under this regime, metal-to-metal contacts are commonplace despite the presence of the lubricant film. This might lead to the propagation of cracks within the metal sub-structure and catastrophic failure of a lubricating film, resulting in dramatic increase in friction and wear. High viscosity oils and two types of lubricity additives are used to prevent such failures: 1) barrier lubricants and 2) Extreme Pressure (EP) additives. The former type functions by creating an easy-shear layer between the moving surfaces, which is resistant to normal direction of loads due to the sheet-like morphology of the barrier lubricants: graphite, Mo_2S, hexagonal BN, mica, etc. EP-type additives function by inducing a chemical reaction

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under high interfacial pressures and elevated temperatures between the oil and metal, subsequently creating an intermediate layer, capable of primarily reducing friction. Most often sulfurized, chlorinated and phosphated compounds are used as EP additives. It has been assumed [1] that these additives are 'activated' by the heat on the surface and then react with iron. Sacrificial layers of iron sulphides, chlorides or phosphates resp. are formed, a. k. a. tribofilms, which protect the surface. The temperatures, necessary for the tribofilm formation to begin, the nature of EP additives and the lubrication regime have remained a matter of speculation.

Arrival of analytical techniques, based on X-ray spectroscopy, in particular X-ray photoelectron spectroscopy (XPS), highlighted the complexity of formation mechanisms of EP tribofilms. ZDDP tribofilms have been investigated in detail [2], with some research carried out on sulfurized [3–5] and chlorinated [6, 7] EP additives. Carbonaceous layers were not investigated as much, mostly because of various complexities. Much slower removal rates of carbon atoms, compared to other elements, by Ar-ion sputtering, which is often used in tandem with XPS, are pratically problematic [4]. The understanding of ZDDP deposition mechanisms is rapidly improving for elastohydrodynamic and mixed lubrication conditions, but remains perplexing when boundary lubrication is considered. ZDDP is also often used as an EP additive, although in boundary lubrication regime it is viewed as less effective in preventing high friction and lubrication failure than chlorinated EP additives [9]. Tribochemistry of chlorinated hydrocarbons (waxes, paraffins, olefins), which are considered the most effective Extreme Pressure additives [6, 7, 10, 11], has been investigated much less because in many countries the CP usage is restricted. It is widely assumed that on steel CP forms a chloride layer, which acts as a sacrificial film to prevent major surface damage [12, 13]. This perception has been occasionally questioned by the lack of correlation among CP homologues [7, 10]. Formation of carbon-rich morphologies on the top steel layers has been proposed [6, 10] to explain the lubricity of CP additives. Nevertheless, the boundary lubrication mechanisms of CP remain quite uncertain. The effects of base oils are rather confusing as well, even comparing ester-based formulations to those of mineral oils, the latter demonstrating better [14] or poorer lubricity [15–17]. Vegetable oils are more widely considered as diluents in lubricants [18] due to price convergence with mineral oils and improved lubricity. Consequently, a better understanding of their role in boundary lubrication tribochemistry is much more necessary.

Earlier studies [19–22] established that under high interfacial pressures it was necessary to add much less EP into ISBO to achieve good boundary lubrication performance compared to IPMO. The experiments employed two tribotests: a standard Four Ball EP test [23] and the Twist Compression Tribotester (TCT), in which several regimes were utilized. It must be pointed out that all the tribotests were quite short in duration, lasting approx. 1 minute. Blends of ZDDP and CP additives in ISBO demonstrated clearly better

lubricity than those in IPMO. Several possible explanations were discussed, relating to previous studies of boundary lubrication: 1) rheology differences of the base oils [24], 2) different adsorption rates of EP additives on steel surface [22], and 3) the ability of the base oil itself to form tribofilms [6, 10]. This study focuses on the formation of nano-sized layers under short-term boundary lubrication conditions in trying to explain the reported observations.

One of the most basic techniques for surface layer analysis is XPS. This instrument has been used to determine elemental composition of the 3–5 nm top layer of the wear track. Elemental compositions of deeper layers can also be determined utilizing argon-ion sputtering to gradually remove surface material between XPS analyses. Such an approach has been used numerous times to study ZDDP tribofilms, whose structure and composition have already been established with relative certainty [2]. This cannot be said about their formation mechanisms, because ZDDP forms tribofilms in a quite complex manner.

In this experimental study, in line with the previous methodology [19], TCT was used at 200 MPa load for fixed durations of 10 seconds to achieve steady friction conditions of boundary lubrication. Soy (soybean) oil, as one of the major vegetable oils, and paraffinic mineral oil 150N of similar viscosity were used as sources of ISBO and IPMO base oils for CP and ZDDP additive formulations. XPS in tandem with Ar-ion sputtering and microscopy techniques were employed to investigate the surfaces of TCT wear tracks and compare the EP additive concentration effects on the early stages of boundary lubrication.

EXPERIMENTAL

The same materials were used as in previous studies [19–22]. Conventional alkali-refined food grade soybean oil (0.92 g/mL, 32 cSt at 40 °C; FFA < 0.5 mgKOH/g; Iodine Value 130 cgI$_2$/g; H$_2$O < 0.1%) was manufactured by ADM (Decatur, IL), solvent refined low sulphur paraffinic ISO VG 32 mineral oil (0.86 g/mL; 30 cSt at 40 °C and 5.5 cSt at 100 °C; pour pt <−9 °C; S < 0.1%, H$_2$O < 0.02%) by American Refining (Bradford, PA), liquid t-butyl substituted phenolic antioxidant (CAS RN 2082-79-3, 98% purity) by Ciba Chemicals (Tarrytown, NY), chlorinated paraffin (CP), CAS RN 63449-39-8 (1.3 g/mL, chlorine contents 53 wt. %, 850 cSt at 40 °C) by Dover Chemical (Dover, OH), zinc di-ethylhexyl dithio phosphate (ZDDP), CAS RN 4259-15-8, (1.15 g/mL, 9.5% Zn, 8% P and 16% S, all by wt.) by Rhein Chemie (Trenton, NJ). Molecular structures of CP and ZDDP are shown in the Scheme. Analytical grade heptane and acetone solvents were used for cleaning. Oxidative resistance of biobased oils is poor [25], mineral oils also exhibit significant degradation, if placed in thin films [26]. Therefore, all formulations (with and without EP additives), including those of mineral oil, were inhibited by blending with 0.5% AO. All blends were clear and homogeneous and their percentages are expressed
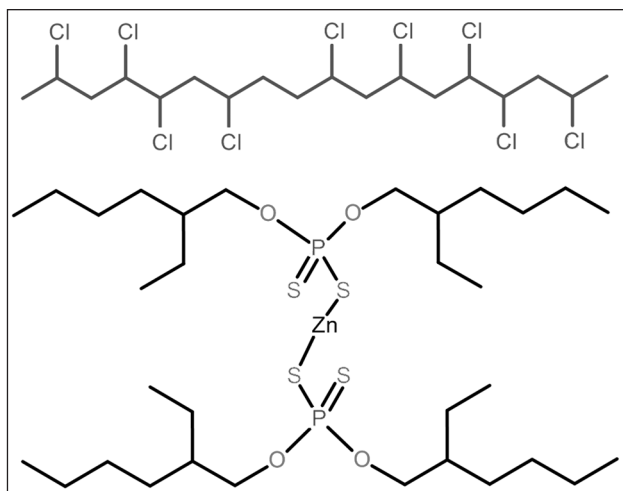
Scheme. Molecular structures of chlorinated paraffin (CP, top) and zinc di-2-ethyl hexyl dithio phosphate (ZDDP, bottom). CP also contains large amounts of numerous isomers and longer C chain homologues

"weight-to-weight", i. e. wt. %, rather than vol. %, unless indicated otherwise. Please note that occasionally atomic percentages (at. %) are used to characterize elemental compositions. In some tabulations "n. d." is denoted to show that the data was "not determined".

A TCT machine, manufactured by TribSys LLC (Valparaiso, IN), was used at the same conditions as previously [19] with the rotation speed of 10 rpm (1.2 cm/s) and the load of 200 MPa. The annular cylinders (used as "twisted" surfaces in TCT), supplied by Ban-FAM Industries, Inc. (Cleveland, OH), were made of tool steel (high chromium D2: 1.55 C, 0.3 Si, 0.4 Mn, 11.8 Cr, 0.8 Mo and 0.8 V, as specified by the supplier, all in wt. %) 60–65 R_c hardness, surface roughness R_a 0.15 μm. Flat workpieces 35 × 100 × 0.8 mm (used as stationary surfaces in TCT), supplied by ACT Test Panels (Hillsdale, MI), were made of cold-rolled steel (SAE 1008/1010; 0.13 max C and 0.25–0.60 Mn as specified by the supplier, both in wt. %). Each oil sample of 0.7 to 1.0 ml was evenly spread onto the cleaned and degreased side of the workpiece using a pipette.

The TCT tests were run in the fixed duration regime of 10 s ± 0.5 s (or 4 s ± 0.5 s in case of IPMO w/o EP additives) after the initial engagement of the surfaces. Usually it would take 0.5 to 1.0 s to achieve 90% + of nominal load value, depending on the thickness and rheological properties of the oil film as well as the ambient properties (temperature, mechanical efficiency of the hydraulic system in the equipment, etc). This is different from the Time-to-Failure (TTF) regime where the run durations last until lubricant film failure: sudden increase in friction and catastrophic surface damage (Fig. 1), as described previously in more detail [19]. In order to avoid flash corrosion due to the CP blends [9], the wear tracks on flat sheets after the TCT test of CP blends were thoroughly degreased with heptane and acetone by rinsing. Then these sheets were coated with IPMO or ISBO without EP additives, depending on the base oil of the sample, while wear tracks of oils without EP additives or ZDDP blends were

not degreased after the TCT test. Afterwards, the workpieces were wrapped in plastic to keep them for several weeks until the surface analysis study. Immediately before the surface analysis, all workpieces were washed again by sonicating them in acetone, followed by sonication in heptanes.

An atomic force microscope (AFM), optical microscope, profilometer and XPS were used for the wear track analysis. The XPS instrument PHI 5600ci (Physical Electronics) with monochromatic Al Kα X-rays was used with an analyzer pass energy of 58.7 eV. An argon ion sputtering gun attached to the XPS chamber was used for removal of the surface material at about 6–8 nm per 1 minute. The TCT workpiece was unwrapped, a segment was cut off with metal shears, thoroughly washed with heptane and acetone in an ultrasonic bath (15 min sonication each), dried and transferred to the XPS instrument for analysis in less than 1 h. One TCT wear track was tested two times, using the XPS/Ar sputtering sequence and the depth profiles of the elemental concentrations were reproduced with higher than 95% accuracy. Elemental concentrations were calculated from XPS peak areas using sensitivity factors provided by the instrument manufacturer. The AFM study was carried out on a Perkin Elmer JVOX instrument. A digital optical microscope Motic (Sony, Japan) was used at 50 × magnification. A "Ppophilograph type 252 GOST 2789-73" was used (Moscow, Russia) to determine the roughness parameter R_a as described [27].
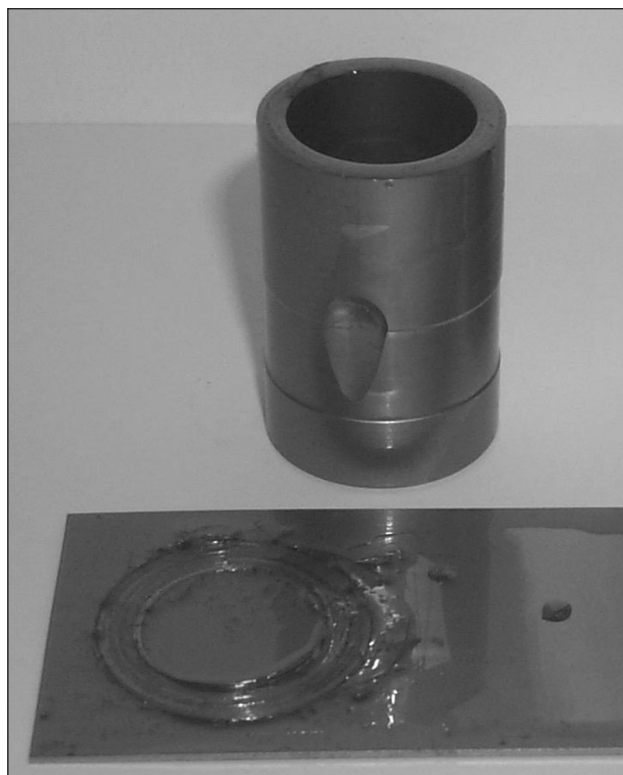

Fig. 1. Photograph of wear tracks after time-to-failure (TTF) determination at 200 MPa: inverted annular cylinder (top), made of tool steel, and workpiece (bottom), made of low carbon steel. Wear scar is visible only on the workpiece due to its much lower hardness and poorer strength

RESULTS AND DISCUSSION

Earlier studies investigated the friction effects of ZDDP and CP in IPMO and ISBO in greater detail [19–22]. This study focused mostly on analysis of nanosized layers, formed as a consequence of high interfacial pressures and short-term tribological interactions under TCT conditions. In this test the surfaces are brought into contact dynamically: the steel annulus is rotating when gradually engaging with the steel panel, i. e. it is first "twisted" and only then "compressed". Thus the steady state regime is attained without the transition through the severe static friction phase. Such a mode of engagement brings the surfaces into boundary lubrication conditions through the course of less than 1 s. The time needed to establish high interfacial pressures (90% + of nominal value) is not counted towards the effective run duration, which is 10 s in this study.

It must be noted that TCT operates under 'starved film' conditions, when the lubricant is not replenished in the friction zone. Under such conditions the access to lubricant from the outside is minimal and the film replenishes itself only from the oil, accumulated in the asperity 'valleys' via diffusion mechanisms, rather than forced entrainment. Since a larger number of deep valleys might assure better film replenishment, the surface texture is extremely important. In this study, the surface preparation of TCT specimens was carefully controlled both for the workpiece and for the annular cylinder. It must also be noted that TCT has good heat removal ability from the lubricating interface due to the relatively large metal anvil, which is pressed against the workpiece. A large surface area of cold metal and short testing durations reduce the uncertainty of thermal stress influence on EP additive and base oil degradation, metal oxide formation and amplify the significance of tribochemical mechanisms with respect to conventional thermal / catalytic reactions.

In selecting the TCT test duration, the torque-vs-time plots were used, with torque converted into the coefficient of friction. As discussed previously [12, 13, 19, 28], certain torque fluctuations are unavoidable during the test, especially when the surface damage becomes pronounced. In this study, the CP and ZDDP blends in mineral oils are able to assure quite long steady-state operation at 200 MPa, see Fig. 2.

It can be seen from Fig. 2 that in the presence of EP additives the formulations show quite similar frictional tendencies. After the surfaces are engaged and the static friction effects are reduced, the torque goes down until the nominal load is attained and the lubrication regime shifts to more severe boundary lubrication conditions. When the interfacial pressures stabilize, the friction stabilizes as well due to the development of a lubricious film. The duration of relatively stable, gradually increasing friction depends on the ability of the lubricious film to prevent excessive wear under starved conditions. Once the wear rate increases, the surfaces can no longer stay separated by the film and catastrophic damages start extending into the metal substrate. This becomes evident by the increase in friction torque, along with pronounced vibrations, noise generation, rapid heating and metal shredding, which can be observed on the workpiece (Fig. 1). Time-to-failure (TTF) represents the ability of such film to withstand given boundary lubrication conditions [12, 13, 19, 28].

Frictional characteristics of these blends (Fig. 2) have been tested previously [19–22] and determined TTF corre-
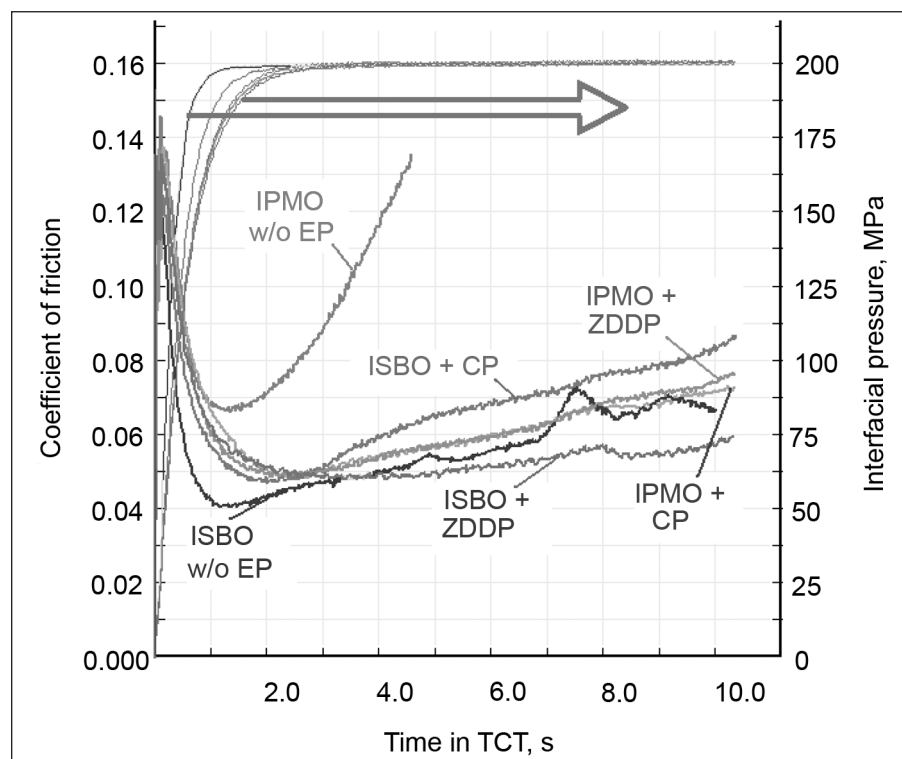

Fig. 2. Development of interfacial pressures and coefficients of friction during the course of TCT runs. Recorded data includes low pressure start-up periods, which are disregarded when establishing effective 10 s TCT durations
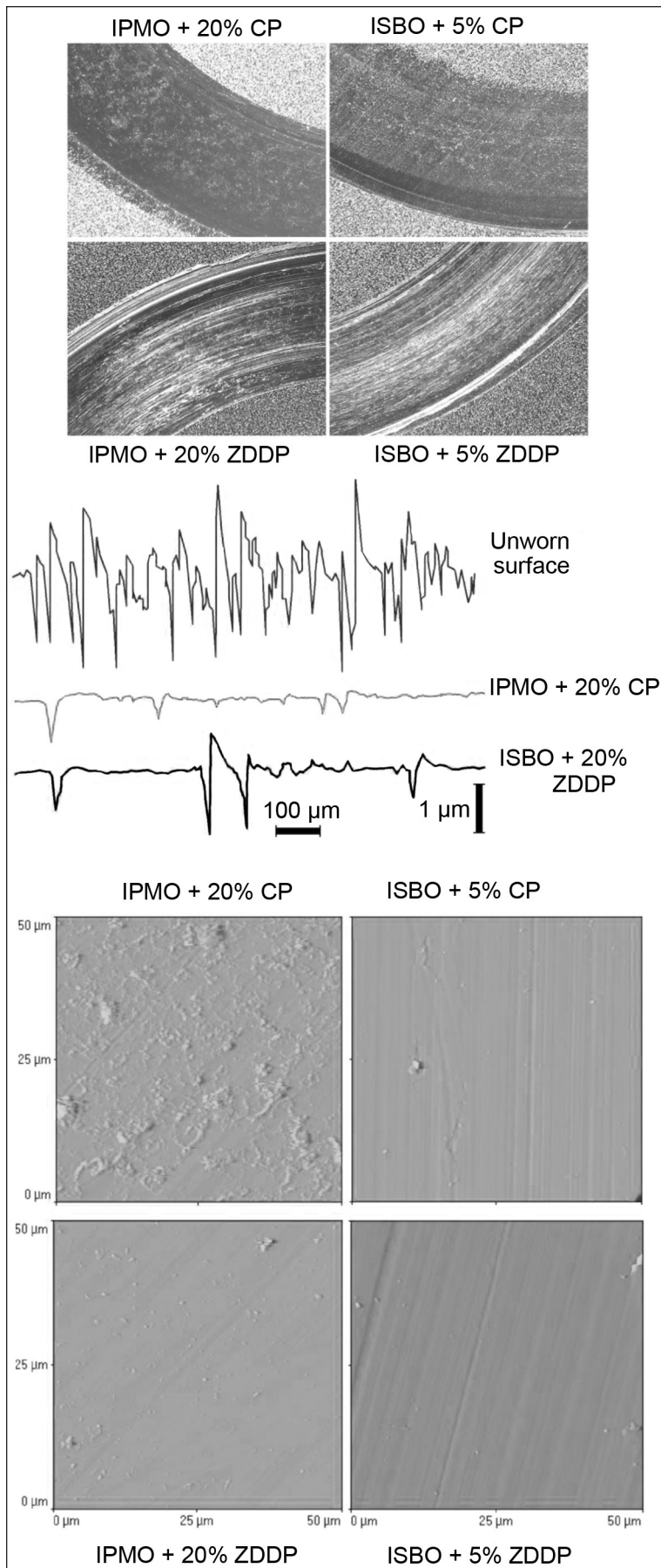
Fig. 3. Surface photomicrographs, profiles and AFM images for selected wear tracks

lated quite well with the weld points of the Four Ball EP tribotester. This shows that the steady-state boundary lubrication conditions are somewhat similar between the tests, despite major differences in the friction zone conditions (pressure gradient linearity, velocities, oil entrainment, etc.). The previous study has also yielded a very technologically important conclusion that the nature of the base oil affects the EP additive performance very significantly, especially during the early stages of boundary lubrication. As a result, biobased oil formulations require only half as much of additives, compared to mineral oil based formulations [19].

As apparent from Fig. 2, 90% of nominal interfacial pressure in TCT is almost always attained within less than 1 s of surface engagement. In this study, 10 s duration was selected to produce the wear tracks for subsequent determination of changes in the elemental composition of steel surface. The only exception was IPMO without EP additives, which was run on TCT for 4 s due to its very low TTF and questionable ability to form a lubricious film at 200 MPa load.

Uniformity of boundary lubrication regime was evaluated by determining the wear tendencies of the samples after the 10 s screening, using a profilometer (Table 1). The actual profilometry measurements with duplicate samples and re-runs along with standard deviations can be found elsewhere [20, 21]. TTF results from previous reports [19] were processed in the same manner as the profilometry data and also included in Table 1. Correlation between these two parameters is not apparent, moreover, the repeatability of R_a is poor due to the occasional microwelding. It is not unusual in TCT to experience metal pickup under high loads [12, 13] in the areas where a lubricious film does not develop or its failure occurs prematurely due to surface preparation defects, metal microstructure or other factors. Consequently, a number of grooves are formed even within 10 s duration (Fig. 3). The photomicrographs show that the worn surfaces have several grooves, formed because of microwelding. This is even more apparent in the surface profiles. Due to the relatively low number of total grooves, the appearance of several additional deep grooves results in significantly higher R_a value, as can be deducted from Table 1. When plain ISBO, ISBO + 5% CP and IPMO + 20%

Table 1. **Profiles of wear tracks, lubricated with 0, 5 or 20 wt. % EP additive (CP and ZDDP) blends in mineral (IPMO) and soybean (ISBO) oils, after TTF determinations**

Additive, wt. %	Range of time-to-failure (TTF), s		Range of roughness, Ra	
	ISBO	IPMO	ISBO	IPMO
w/o EP additive	19–24	3–5	0.30–0.48	0.24–0.41
5% CP	16–39	n. d.	0.30–0.75	n. d.
20% CP	35–79	11–36	0.30–0.53	0.24–0.39
5% ZDDP	39–49	n. d.	0.27–0.43	n. d.
20% ZDDP	18–38	15–17	0.22–0.64	0.23–0.65

ZDDP were tested 2 times on TCT for 10 s, significant variation of R_a was observed. Nevertheless, the wear damage was on the same order of magnitude for all the samples, including IPMO and ISBO without EP additives.

These observations indicate that the selected tribotesting parameters (10 s in TCT under 200 MPa) produced relatively stable friction conditions among all IPMO and ISBO blends with CP and ZDDP. The wear regime could be considered qualitatively similar and represented typical initial stages of severe boundary lubrication. Although none of the EP blends were capable of preventing surface wear effectively, none of the samples (except IPMO w/o EP adds) showed lubrication failure within 10 s either. To the contrary, the wear damage to the surface after TTF determination (Fig. 1) was not within fractions of a micron, but rather on the order of millimeters. This illustration shows that wear tracks from TCT runs of 10 s durations were still far away from the lubrication failure.

Elemental composition of wear track surfaces
XPS was used for the analysis of the elemental composition of the tested TCT panels. It must be noted that the test lubricants were thoroughly washed off the wear tracks with acetone and heptanes via sonication before analysis. Consequently, most likely some loosely-attached semisolid layers were removed during the wash-off. However, it was very important to eliminate as much residual lubricant as possible, because otherwise the elemental composition of the lubricant itself would interfere with the determination of elements in the produced nano-layers. Significant roughness of the wear tracks and unworn surfaces in particular was a major obstacle in trying to remove the residual lubricants and an aggressive wash-off procedure was therefore necessary. As a result, the XPS measurements focused on elemental analysis of strongly bound, i. e. chemisorbed and / or reacted tribofilms, rather than on physically adsorbed layers of lubricants.

The XPS analysis found detectable quantities of the elements from EP additives not only on the wear tracks, but also on unworn surfaces. In addition to Zn, S, P and Cl, which originated mostly from ZDDP and CP, other detected elements included Fe, C and O. The measurements showed that ZDDP and CP produced quantifiable amounts of Zn (Table 2) and Cl (Fig. 4) resp. both on the unworn surfaces and in the wear tracks. Their signal-to-noise ratio was relatively weak, but still sufficient to draw semi-quantitative comparisons. Since both ZDDP and CP are known to adhere strongly to the surfaces, it is not surprising that they could not be washed off completely from the unworn workpiece segments. The ZDDP data in Table 2 shows that Zn contents on unworn metal is higher than that in wear tracks for all three tested blends despite quite aggressive wash-off procedure. Qualitatively, this observation could also be extended to S and P, however, the signal-to-noise ratio in case of the latter two elements was much closer to the detection limits and the measurement repeatability was not acceptable.

Such findings suggest that a simple ambient exposure of steel surface to ZDDP blends without any friction is more likely to produce additive films on the metal than short-term severe boundary lubrication conditions. This observation is somewhat counter-intuitive, because it is widely perceived that ZDDP forms substantially thick (~100 nm) and durable tribofilms [2]. However, it must be kept in mind that 10 s TCT duration is relatively short, while most ZDDP film studies are carried out in the settings where the surface had been exposed to friction zone conditions for much longer durations. In addition, the TCT friction zone conditions undoubtedly represent severe boundary lubrication, while ZDDP tribo-

Table 2. **Influence of ZDDP concentration on zinc contents (at. %) as determined by XPS (without sputtering) in wear tracks after 10 s TCT**

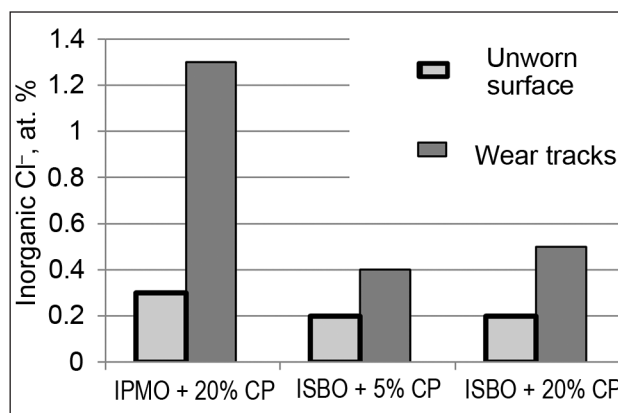|	Unworn surfaces, Zn at. %	Wear tracks, Zn at. %
ISBO + 5% ZDDP	0.5	0.3
ISBO + 20% ZDDP	0.8	0.5
IPMO + 20% ZDDP	0.8	0.6

Fig. 4. Inorganic Cl atom content (at. %) on wear tracks from XPS measurements (without sputtering) before and after 10 s TCT runs

films are more widespread under milder lubrication regimes, such as elastohydrodynamic.

It must be emphasized that Zn, S and P were detected only in the top 5 nm of the surface. Concentrations of Zn, S and P receded below detection limits (BDL) of XPS after 60 s Ar-ion sputtering, which would represent 6 nm depth on a flat surface. Again, this confirms that during the 10 s TCT run detectable S or P-containing nano-layers were not produced in the wear scars. Very likely, most of the EP additive elements were present on the surface due to conventional chemisorption, rather than tribochemical reasons. During Ar-ion sputtering it was also observed that elemental oxygen is nearly absent within the steel substrate, being present only on the surface, just as Zn, S or P.

When analyzing the wear tracks after TCT tests of CP blends, chlorine levels were higher than those on the unworn areas, an opposite tendency than that in ZDDP blends. After 30 s of Ar-ion sputtering, which represented the removal of 3–4 nm of the surface layer, only traces of Cl were found and they completely disappeared after the second round of sputtering. Along with Cl atoms, elemental oxygen also disappeared with sputtering, unlike Fe or C. Nearly complete absence of Cl below the very surface of the wear tracks was no less surprising than the absence of Zn or S in case of TCT tests with ZDDP blends. With high contents of organic Cl in ISBO and IPMO blends, one can reasonably expect substantial amounts of inorganic chlorides to be formed under severe boundary lubrication conditions. However, XPS observations demonstrate that the chloride formation processes do not dominate during the early stages of boundary lubrication.

Nevertheless, more Cl was retained on the surface after the 10 s TCT runs than on unworn surfaces. In contrast to ZDDP, whose conventional adsorption is more pronounced under friction free conditions than under boundary lubrication conditions, CP is more likely to be involved in tribochemical reaction on the surface. Sputter profiling showed that all Cl was contained in the top 5 nm of material on the metal surface. XPS analysis before sputtering showed two sets of Cl 2p peaks; each set being comprised of a doublet with splitting of 1.6 eV. The set of peaks with $2p_{3/2}$ binding energy of 198.6 eV was assigned to inorganic chloride (ferric or ferrous chlorides) and the set of peaks with the $2p_{3/2}$ binding energy of 200.6 eV was assigned to organically bonded Cl (as in CP). More details on the curve-fitting technique along with the figure of Cl 2p spectra could be found in the previous report [20]. The quantitative XPS data on Cl contents was acquired from the top surface layers without sputtering. Along with unworn surfaces, the Cl contents were quantified on the wear tracks from TCT runs with 5% and 20% CP blends in IPMO and ISBO (Fig. 4). The results show that IPMO blends resulted in higher chloride contents on the surface, than with ISBO, the latter being only slightly higher than the limit of detection. Nevertheless, these results suggest rather different tribochemical mechanisms of CP formulations in IPMO and ISBO.

Relatively low, albeit quantifiable, amounts of strongly adhered Cl on the surface cannot be considered as the evidence of tribofilm formation on the surface during the 10 s TCT run. It might be possible that a chloride layer is formed, however, similar Cl amounts can be caused by isolated chloride crystals, bound to the peaks of asperities, or some chloride deposits in the valleys between asperities, or some chloride pockets in the metal. Although the presence of chlorine-rich tribofilm cannot be proven, the evidence of tribochemical reaction between CP and the steel surface is quite convincing, at least in the case of IPMO + 20% CP. The duration of 10 s is sufficient to heat up the bulk steel panel only slightly. In the friction zone the localized hot spots might reach high temperatures and it is known that reaction rates of most hydrocarbons or esters double with every 10 °C increase [25]. Consequently, the supposition that during the 10 s tribotest a quantifiable amount of 1.3 at. % Cl adheres strongly to the steel surface solely due to thermal / catalytic mechanisms without any assistance of tribochemical reactions becomes less convincing.

In contrast to Zn, Cl, P and S measurements, C content on the surface was very high, 60 at. % or higher. Intuitively, such high amounts of carbon can be attributed to organic matter, still present on the surface after the residue wash-off procedure. However, the initial exercise by Ar-ion sputtering showed that within deeper layers of the steel substrate C levels do not recede nearly as rapidly as those of Cl or Zn. Therefore, a more extensive XPS and sputtering study was carried out specifically to determine C contents within the steel substrate.

Depth profiles of % carbon

The wear tracks with average surface roughness R_a of 150 nm present a challenge for the analysis based on XPS in tandem with Ar-ion sputtering. The parameters for Ar sputtering, employed in this study, were set to remove 1 nm of atomically flat surface in 10 s of the sputtering process. However, in the presence of asperities, whose height exceeds the thickness of the removed layers by at least an order of magnitude, it is questionable whether the removal of the top layer material proceeds uniformly throughout the surface. Depending on the impinging angle of Ar-ion stream, the rate of material removal might be lower in the valleys of asperities, compared to their peaks. In this study no attempt was made to verify the accuracy of the relationship between Ar sputtering duration and the thickness of removed layers.

The surfaces were subjected to very thorough residue wash-off via sonication, nevertheless, the residual amounts of organic matter were still the most likely reason of high C contents on the unworn surfaces. Many investigations showed how difficult it was to remove esters from metal surfaces [29, 30]. XPS studies by another research group found high C contents on unworn surfaces in somewhat similar settings [31] despite aggressive wash-off as well. Carbon containing residues could not even be removed by prolonged

Table 3. **Recession of carbon contents (at. %) as determined by XPS due to Ar-ion sputtering in wear tracks (10 s TCT, 4 s in case of IPMO w/o EP)**

Oil	EP additives	Duration of Ar-ion sputtering, s						First BDL, s
		0 s	30 s	60 s	120 s	180 s	240 s	
ISBO	w/o EP	57	9	3.7	2.5	n. d.	n. d.	150
IPMO	w/o EP	69	6	5	n. d.	n. d.	n. d.	90
ISBO	20% CP	70.5	24	14	7.3	5.8	3.6	360
IPMO	20% CP	72.5	12	8	6	n. d.	n. d.	150
ISBO	20% ZDDP	73	20	14	10.5	8.0	BDL	240
IPMO	20% ZDDP	73	12	8	4	BDL	n. d.	180

Ar-ion sputtering from unworn surfaces, most probably due to a very rough surface profile. The roughness in the proximity of 4 μm R_a created very favourable conditions to host pools of residual oil in valleys and crevices. Consequently, C content values fluctuated greatly on unworn surfaces as determined by XPS with or without Ar-ion sputtering and therefore are not supplied in this report. However, wear tracks were much smoother than unworn surfaces (Fig. 3). Consequently, in wear tracks the values of C contents were much more reproducible and lead to a number of interesting observations.

Another challenge in C contents determination is presented by the presence of carbon in steel as an alloy component. Just 0.1 wt. % C contents translate into 4 at. % C contents in the employed SAE 1008/1010 steel, whose max C specification was 0.13 wt. %. Therefore, all XPS readings of C contents at 5 at. % and less might mostly originate from the steel substrate, rather than tested lubricant formulations.

Nevertheless, C contents were more substantial than 5 at. % even for samples which perform poorly under boundary lubrication conditions, such as ISBO without EP additives (Table 3). Although the abundance of carbon recedes rapidly within the first 30 s of Ar-ion sputtering, the residual C levels are still significant. Such unexpectedly rich carbon amounts quite deep into the metal substrate are even more surprising than the above observation of nearly complete absence of Cl or Zn below the metal surface. The car-

bonaceous nature of the top layers can hardly be explained by the residues of organic matter in the wear tracks after the extensive residue wash-off procedure. It is unlikely that C presence is a result of strongly adhering organic films. If the residual organic matter were not washed off completely and were not removed after the extensive sputtering, then elemental analysis would register significant amounts of Zn and S. However, the blends with 20% ZDDP did not show any Zn present after just 10 s of the sputtering, while the C contents were not reduced more significantly than by 1/3 (Fig. 5). Further sputtering showed that the C content decreases when going deeper into the substrate. However, carbon levels were clearly present after more than 100 s sputtering for most of the samples (Table 3).

Before Ar-ion sputtering, the levels of C on the surface were recorded at 59–75 at. %, but these values are highly affected by the extent of surface cleaning. Thus the C content on the surface should only be considered in a qualitative manner. Nevertheless, high surface carbon content suggests that the organic material forms chemical bonds with the steel surface on the very top layers. Due to rapid reduction of C contents with sputtering, it can be suspected that an organometallic monolayer is likely, but this supposition is speculative considering relatively high surface roughness. It is, however, in line with the observations by several research teams [3], who have found organometallic compounds on the steel surface. The layers of steel substrate below the surface contain less carbon, but its abundance is still appreciable and suggests that carbonaceous components might penetrate well beyond 10 nm into the metal matrix. Zn or Cl are not present in their vicinity, suggesting that base oil molecules and not EP additives are more actively involved in the layer formation. This scenario is further fortified by the observation that biobased oil (ISBO) formulations produce undoubtedly thicker carbonaceous layers, compared to mineral oil (IPMO).

Thicker tribofilms would convincingly explain the previous observations [19–22], showing that biobased oils need much lower treat rates of EP additives for achieving a given performance under boundary lubrication. The previous TCT study [19] found that base oil (ISBO vs IPMO) influence on TTF was as significant as that of EP additive concentrations. Twice as much EP additives were needed in mineral oil to achieve a comparable TTF as that of a vegetable oil formulation. This study, however, does not provide evidence that a continuous nanolayer of organometallic or other types of
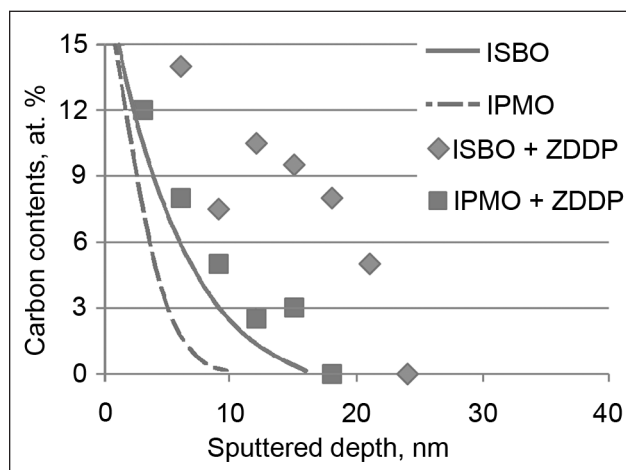

Fig. 5. Influence of 20 wt. % ZDDP on carbon contents within the worn substrate. XPS C amounts (at. %) vs estimated depth profiles of wear tracks after 10 s (4 s in case of IPMO w/o ZDDP) runs in TCT

metal / carbon compounds (such as iron carbides or carbonyls) form on the surface. Therefore, it is premature to suggest that a carbonaceous tribofilm is formed early into the boundary lubrication conditions. High surface roughness hinders the topographic resolution, thus random carbonaceous inserts (e. g. graphite), localized iron carbide agglomerates and other non-uniform structures might produce readings, similar to those of a continuous uniform film. Therefore, a less descriptive term 'nano-layer' is preferred in this report. This study can be viewed as a screening evaluation of elemental contents of the top surface depth profile in order to highlight the influence of separate lubricant components. For more detailed assessment, the load levels and the substrates need to be chosen in such manner that lower surface roughness is produced under similarly severe boundary lubrication conditions. Smoother surfaces would make the tribologic structures easier to characterize.

The study findings show that the role of Zn, S or Cl might be less significant than that of the base oil in controlling friction under boundary lubrication conditions. These elements are nearly absent below the surface, while the amount of C is significant even deeper than 10 nm not only in case of ZDDP formulations, but also using CP as an EP-additive and even plain base oils (Figs. 5, 6). ZDDP or CP are unlikely sources of C deep into the substrate, while C origination from the base oils is much more probable. Nevertheless, these EP additives are clearly beneficial to the lubricity under boundary lubrication conditions. It is also evident that C penetrates much deeper into the substrate, when ZDDP or CP are used in the formulations (Figs. 5, 6). Please note that in the latter charts C contents gradient for samples w/o EP additives is represented by the trendlines, derived using the data from Table 3. This suggests that EP additives help forming a thicker nano-layer, which assists in boundary lubrication. Also, Zn or Cl undoubtedly can be detected on the top surface even after vigorous cleaning, which suggests that EP additives initiate

some chemical processes on the metal surface. They do not penetrate far into the substrate; however, their presence on the surface might contribute significantly to the friction reduction.

A notable observation is the fact that the carbonaceous layer forms in only 10 s duration of TCT run. Its formation probably begins even much sooner than that, since IPMO run for 4 s shows a very similar carbonaceous layer formed already. Continuation of TCT run to 10 s was not possible with the IPMO sample because major surface damage begins at 6–7 s duration. More accurate determination of the formation kinetics of carbonaceous nano-layers would require a separate specially designed study with shorter increments of boundary lubrication and possibly lower loads as well as surfaces with less roughness. Nevertheless, the findings, which show that ISBO leads to much thicker carbonaceous nano-layers under boundary lubrication conditions, compared to IPMO, strongly encourage more widespread application of biobased oils as lubricants for high interfacial pressure applications.

CONCLUSIONS

Boundary lubrication experiments, using biobased oil ISBO and mineral oil IPMO formulations with CP and ZDDP additives, were performed, followed by surface analysis using XPS with Ar-ion sputtering. On low carbon steel surfaces the following findings were revealed.

• During early stages of boundary lubrication, Zn and S as well as Cl can be found only on the very top surfaces in ZDDP and CP formulations, respectively.

• In 10 s or less under boundary lubrication conditions a carbonaceous layer is formed on the surface.

• Much thicker carbonaceous layers are formed with ISBO rather than IPMO, explaining why only half as much EP additives are necessary to reach the same boundary lubrication performance in biobased oil blends compared to mineral oil blends.

• Formation of inorganic chlorides on steel surfaces under severe boundary lubrication conditions was evident only in mineral oil blends and not in biobased oil.
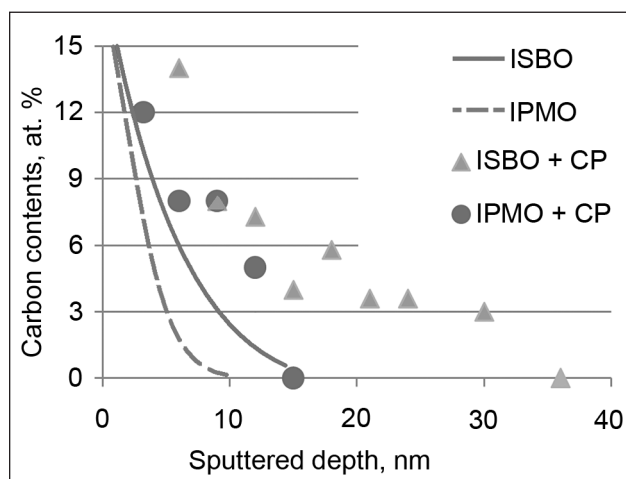
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Fig. 6. Influence of 20 wt. % CP on carbon contents within the worn substrate. XPS C amounts (at. %) vs estimated depth profiles of wear tracks after 10 s (4 s in case of IPMO w/o CP) runs in TCT

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ANGLINGŲ NANOSLUOKSNIŲ FORMAVIMAS ESANT AUKŠTIEMS SLĖGIAMS TARP PAVIRŠIŲ, TEPAMŲ MINERALINĖMIS IR BIOLOGINĖS KILMĖS ALYVOMIS

S a n t r a u k a

Siekiant geriau apsaugoti plieno paviršius nuo dilimo esant didelėms apkrovoms, reikia daugiau žinių apie sąveiką tarp tepalų ir metalų aukštuose slėgiuose ir temperatūrose. Cinko dietilditiofosfato (ZDDP) ir chloruoto parafino (CP) 5–20 % masės konc. tirpalai inhibitorių turinčiose parafininėje mineralinėje alyvoje (IPMO) ir sojų aliejuje (ISBO) buvo tiriami sukamojo-slegiamojo judesio tribotesteriu TCT esant 200 MPa slėgiui. Mikroskopu ištyrus dilimo pėdsakus po 10 s TCT, plieno paviršiai buvo žymiai glotnesni nei prieš trintį. Tyrimai rentgeno fotoelektronų spektroskopu (XPS) su argono jonų ėsdinimu parodė, jog minėtų priedų tirpalai ISBO suformuoja kelis kartus storesnius anglingus sluoksnius nei IPMO tirpalai. Nustatyti Cl, P ir S kiekiai buvo nelauktai žemi ir fiksuojami tik iki 5 nm gylio. IPMO paviršiuose CP tirpalai suformavo daugiau neorganinių chloridų nei ISBO tirpalai. Galima teigti, jog bazinės alyvos turi didžiausią įtaką formuojamo anglingo nanosluoksnio storiui esant pradinėms ribinės trinties stadijoms, o ZDDP ir CP įtaka yra ženkli, bet mažiau reikšminga.