

Article

Influence of Artificially Altered Engine Oil on Tribofilm Formation and Wear Behaviour of Grey Cast Cylinder Liners

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Abstract: This work investigates the influence of altered engine oil on the tribological performance, focusing in particular on wear and interconnected tribofilm formation. For this purpose, Zinc dialkyldithiophosphate (ZDDP) additivated engine oils of different degradation levels, produced in an artificial oil alteration process, were used in tribometer tests with a nitride steel piston ring against a grey cast iron cylinder liner model contact. Parameters were chosen to simulate the boundary and mixed lubrication regime typical for the top dead centre conditions of an internal combustion engine of a passenger car. Wear of the cylinder liner specimens was continuously monitored during the tribometer tests by the radio-isotope concentration (RIC) method, and tribofilms were posteriorly investigated by X-ray photoelectron spectroscopy (XPS). The results clearly show that the steady-state wear rates for experiments with altered lubricants were significantly lower than for the experiments with fresh lubricants. XPS analysis on the formed tribofilms revealed a decrease in sulphide and an increase in sulphate states for altered oils evaluated at 120 °C oil temperature, correlating with a decrease in steady-state wear rate. This finding emphasizes the role of sulphate species in the tribofilm formation process and its anti-wear capabilities, in contrast to the sulphide species and the (poly-)phosphate species, as outlined in most of the ZDDP literature. Moreover, the RIC signal that represents the amount of wear in the engine oil showed a decrease over time for specific altered lubricants and test conditions. These “negative” trends in the wear signal are remarkable and have been identified as an incorporation of wear particles from the lubricant into the tribofilm. This finding is supported by XPS results that detected an iron-oxide layer with a remarkably similar quantity within the tribofilm on the surface. Based on these findings, an assessment of the minimum film formation rate and particle incorporation rate was achieved, which is an important basis for adequate tribofilm formation and wear models.

Keywords: wear measurement; radioactive tracers; wear particles; tribofilm formation; ZDDP



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1. Introduction

Zinc dialkyldithiophosphates (ZDDPs) have been used as lubricant additives for more than 60 years and are still an indispensable part of lubrication technology [1–5]. They have antioxidant and anti-corrosive properties, but are best known as effective anti-wear additives, and as such, are in widespread use. After decades of intensive ZDDP research, it is generally agreed upon that under thermal and mechanical (shear) load, ZDDPs, or rather their decomposition products, form a coating on the lubricated surfaces (referred to as tribofilm) that acts as wear protection [6–8]. The structure of this tribofilm, its formation path, and the mechanisms of wear protection it provides have been the subject of numerous investigations [5,8–10] and are by now assumed to be understood at least qualitatively. Recent work has accordingly been concentrating on developing quantitative models for ZDDP tribofilm formation [7,11–13].

In recent years, the detrimental effects of ZDDPs have received growing attention. Exhaust products of ZDDPs are harmful both to the environment and to the operation of catalytic converters, and legal restrictions on the concentration of ZDDPs (or parts of it) are increasingly put into place. This ushered in a surge of research work concerned with reducing (or optimizing) the use of ZDDPs or replacing them altogether with different oil additives [14]. Of late, the oncoming turn to electric or hybrid drive systems, as well as alternative fuel concepts, has become a further incentive to improve the understanding of ZDDP-based wear protection, in order to be able to adapt its use appropriately or develop appropriate replacements [7,15].

One of the points where the optimisation of ZDDP use may be approached is lubricant ageing. Lubricants deteriorate during operation, losing some of their additive content and acquiring contamination, e.g., water or (in the case of combustion engines) combustion products. Research in this area tries to elucidate what influence this has on the effectiveness of the lubricant in the course of its life time [16].

Nagy et al. [15] compared an artificial ageing procedure with aged samples of a commercial engine oil collected from vehicles. Based on conventional oil analysis, they determined the validity of the artificial ageing procedure. Employing this procedure allowed the study of the effects of various parameters, in particular temperature, on the ageing behaviour in more detail than possible from field tests.

In order to achieve the corresponding results more efficiently than with surveys of aged oils from the field, artificial procedures that simulate the ageing of the lubricant on the lab scale have been applied for many years, notably by applying raised temperatures and controlled air flows [15,16]. Recent research in this area has moved in several directions, for instance, considering further ageing-relevant conditions, like adding contaminants, more detailed examination of aged lubricants and their components, or investigation of the tribological effects of oil ageing. Cen et al. [16] investigated ageing of a number of systematic base oil–additive combinations. In addition to standard oil analysis of the aged oils, they were used in a ball-on-disc tribometer test setup and both the tribometric data and the analysis of the tribometer specimen surfaces evaluated. The results not only demonstrate the effectiveness of ZDDP as a very stable antioxidant and anti-wear additive, but also give an indication of the role of ZDDP surface adsorption and decomposition in its anti-wear mechanism.

Dörr et al. [17] used an artificial alteration procedure to study the ageing of a commercial engine oil in general and the degradation of the ZDDP contained in it in detail over the course of several days. Additionally, the altered oils were used for tribological ball-on-disc tests to correlate the artificial alteration with tribometric data and tribofilm formation. The results clearly showed the development of ZDDP degradation products over time and their correlation with tribofilm composition. The tribological performance with the altered oils could likewise be linked to the respective chemical changes.

Besser et al. [18] studied the ageing of fully formulated engine oils with special regard to the effect of mixing bio-fuels into the gasoline. For this purpose, an artificial alteration procedure considering possible combustion products of ethanol was devised. The results showed not only the effectiveness of the artificial lab-based alteration procedure, but also that ethanol combustion products like acetic acid have a pronounced influence on the ageing behaviour of engine oils.

In a recent effort to bring lab-based oil alteration closer to oil ageing in the field, Besser et al. added a nitration step to their artificial oil alteration procedure [19] and compared the altered oils with samples from the field, applying both conventional oil analysis and advanced molecular structural determination. The results show an improved agreement between field ageing and artificial alteration of oils.

In the literature, there are hardly any studies that investigate the wear performance of aged engine oils; most studies usually focus on the performance of fresh oils, only. In particular, there is a lack of information about the wear rates, which are important for the life-time assessment of tribologically stressed components. Coy et al. [20] report that the

decomposition of ZDDP in used oils had only marginal effect on the extreme pressure performance of ZDDP-additivated oils in a four-ball test. Truhan et al. [21] investigated the friction and wear behaviour of fresh and used fully formulated 15W40 engine oil, where different variants of used oil were obtained in different ASTM standard tests. Evaluating the produced oils in a Cameron Plint T-77 test rig resulted, in general, in higher piston ring and cylinder liner wear for the ASTM aged oils. Only one used oil showed less wear for the components than measured with the fresh oil variant. They also concluded that soot and particulate contents had a major effect on the wear of the cast iron in the Cameron Plint test setup. However, these studies are scarce, and the wear rate obtained can be biased by a significant contribution of the running-in wear, since the wear rate is calculated from only two measurements before and after the rather short tests. Furthermore, there is a lack of research that combines the investigation of the wear rates of aged oils with the composition of the tribofilms established on the surface.

Therefore, we used the radio-isotope concentration method in the present paper, which allows measuring the wear online and continuously for an accurate determination of the wear rate, together with surface analytical methods to assess the formation and role of the tribofilms. Artificially altered commercial engine oils in different states of ageing (fresh to fully degraded) are applied in tribometer tests to assess their tribological performance and the effects of ageing thereupon. Apart from the standard tribometry data, wear is measured continuously by the radio-isotope concentration (RIC) method, and the formed tribofilms are analysed with X-ray photoelectron spectrometry (XPS) to correlate the ageing-specific lubricant chemistry with the corresponding tribofilm composition and the tribological data. Running-in wear and steady state wear rate are expected to increase with the oil alteration duration due to the consumption and decomposition of anti-wear additives. This wear behaviour shall be studied in the scope of this work and assessed in combination with the change in tribofilm structure and composition.

The present paper is a stand-alone result in the workflow between [22], which is the preliminary work investigating the impact of the loading conditions for fresh oil lubrication, and the follow-up work of Spiller et al. [23], where the depletion of additives in the lubricant was investigated by changing the lubricants during the tribological testing. Due to personal reasons, Ref. [23] was published before the present paper and thus, the alteration of the lubricants is already described in detail there.

For a clearer understanding of the present work, the main results of the preceding work [22,24] with focus on the necessities of the actual work are summarized as follows:

- The impact of sliding distance, load, and temperature on wear and tribofilm formation with a fresh lubricant have been investigated via a fractional factorial design [24] in these preceding publications. As a consequence, the loading parameters for best differentiation of tribofilm and lubrication regime effects were identified [22] and used as basic loading parameters in the present work.
- SEM, EDX, and AFM analyses of the tribofilms was conducted for investigating the influence of the loading conditions on the tribofilm properties. The tribofilm build-up at the cylinder liner as well at the counter-acting piston ring surface were investigated. The piston ring tribofilm was significantly thinner, obviously due to higher sliding exposure than the tribofilm at the cylinder liner. Further, hardly any material transfer was observed from the cylinder liner onto the piston ring surface [22]. The main mechanisms were found as the formation of a tribofilm in a patch-like structure covering the original surface in the tribologically stressed zone. Scratches in the sliding direction were found on these patches but were not visible on the harder original surface, which was not covered by the tribofilm. This indicates a mild wear mechanism occurring on the original surface. The deposition of a tribofilm in the form of patches on the original surface was also measured by Özkan et al. [14]. Scratches in the sliding direction due to the tribological stress were found in this study on the original surface rather than on the tribofilm, probably due to the higher contact pressures investigated.

- TEM analyses of tribofilms of samples from [23] were analysed in the work [25], indicating the presence of solid iron(-oxide) particles in the tribofilm, presumably due to the wearing process.

2. Execution of Experiments

2.1. General Workflow

The tribological tests were conducted on a linear reciprocating tribometer (SRV4[®]) with a special sample holder for mounting segments cut out from piston rings and cylinder liners. The test parameters on the tribometer were set to simulate the boundary and mixed lubrication regime at the top dead centre (TDC) of a combustion engine, as these are the regimes where the highest wear rates occur for the regarded tribosystem. Differently altered engine oils were used to investigate the influence of oil ageing conditions on wear behaviour. In this context, ageing and altering are used in a synonymous way, as the laboratory process of altering the lubricant aims to mimic the ageing conditions of an engine oil in a combustion engine. Nevertheless, the alteration process in the laboratory may cover most of the effects, but it can be assumed that laboratory alteration does not replace the full range of impacts of a combustion engine.

The wear behaviour was measured continuously by the RIC method for the cylinder liner pieces. The friction coefficient was recorded continuously throughout the test by built-in piezoelectric sensors of the SRV4[®] tribometer. After the tribometer tests, the cylinder liner surfaces were investigated with X-ray photoelectron spectroscopy (XPS) for analysing the chemical composition of the formed tribofilms in comparison to the obtained wear rates (Figure 1).

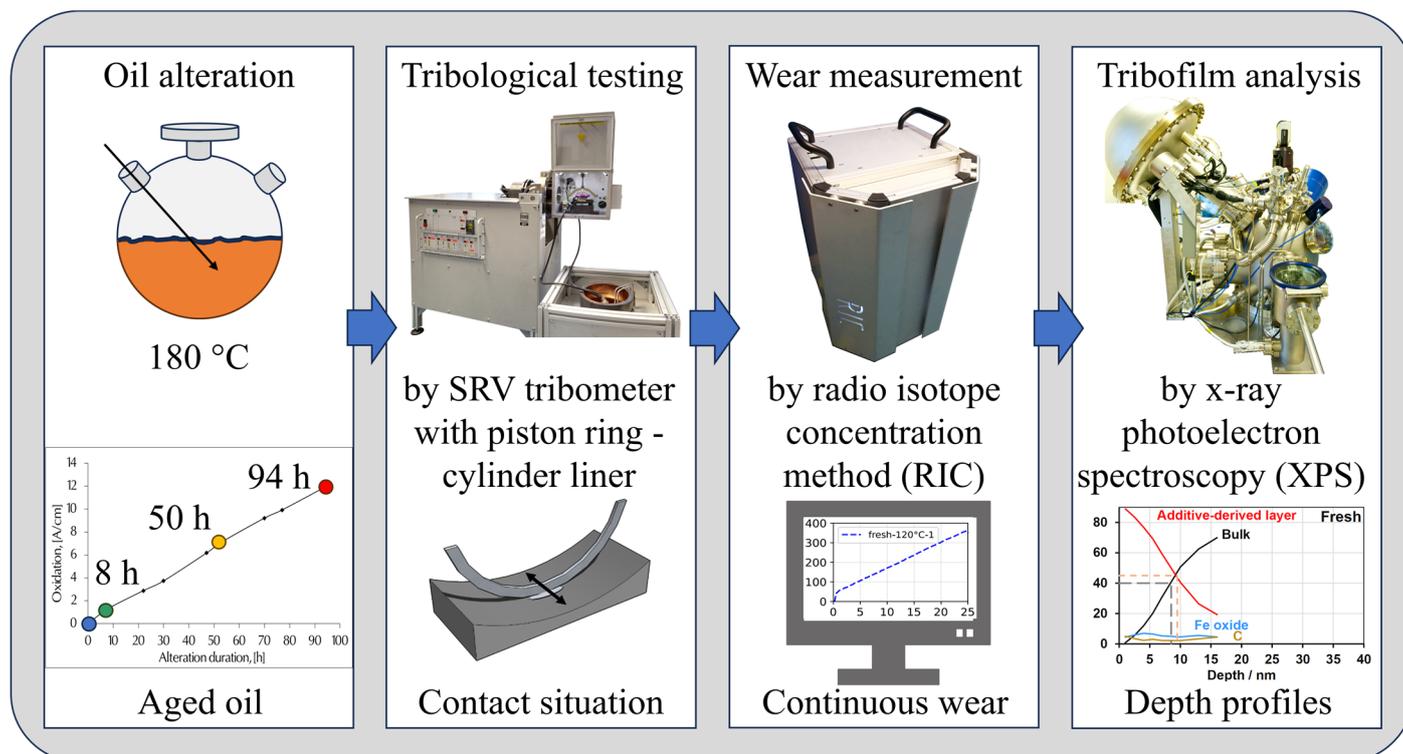


Figure 1. Scheme of workflow, from left to right, of producing altered oil lubricants, running tribological experiments with these lubricants, measuring the wear rate of the cylinder liner pieces, and analysing the formed tribofilms on the cylinder liner surfaces.

2.2. Samples and Materials (Tribocontact)

The specimens used were cut segments of nitrided X90CrMoV18 steel piston rings, and the counterparts were cut segments of grey cast iron cylinder liners of an automotive

grade with graphite in the lamellar form. All specimens originated from real engine components. The chosen materials are commonly applied in internal combustion engines of passenger cars.

The cylinder and piston ring specimens were installed in the SRV4[®] tribometer with a custom-built sample holder [26]. Since the diameter of the piston ring in relaxed state is larger than that of the cylinder liner, the piston ring segment was bent and clamped with the aid of the specimen holder in such a way that the piston ring segment had a radius of curvature approximately 3% smaller than the cylinder curvature. Table 1 shows hardness and roughness properties of the samples used in the wear tests.

Table 1. Material and roughness properties of the samples.

	Piston Ring	Cylinder Liner
Hardness	1200 HV0.05 at the surface 400 HV0.05 in the bulk	235 HV10
Ra roughness value (μm)	0.12	0.19
Rq roughness value (μm)	0.15	0.16

For the investigations in this study, the cylinder segments were activated with Co57 as tracer isotope (also refer to Section 2.6). The piston ring samples were not treated with the activation process. Thus, the RIC wear measurement was focussed on the wear of the cylinder specimens.

2.3. Lubricants and Oil Ageing

The lubricant used in all tests was a fully formulated mineral engine oil, SAE grade 5W-30, with the basic physical and chemical properties shown in Table 2. As can be seen from the tables, the fully formulated oil used in these experiments did not contain any Mo-containing additives (e.g., Mo-based friction modifiers).

Table 2. Basic physical properties of the fresh, fully formulated engine oil SAE grade 5W-30 used in this study, according to Spiller et al. [23].

Physical Properties	
Kinematic viscosity, in mm^2/s	at 40 °C: 56.2 at 100 °C: 9.84
TAN, in mg KOH/g	3.6
TBN, in mg KOH/g	10.5
Anti-wear additive	primary ZDDP
Friction modifier	no
Base oil group	mineral group III oil

The process of artificial oil ageing is referred to in the present paper as lubricant alteration, which is described in detail by Spiller et al. [23] and accentuates the thermal-oxidative stability by exposing the lubricant to dry air and elevated temperatures [27]. The corresponding oxidation values of the oil aliquots sampled during the alteration were used to characterize the ageing state. These were calculated from Fourier transform infrared spectra according to an in-house method [28] that determined the oxidation via the absorption band at 1720 cm^{-1} . For the tribological testing samples, we took ageing durations at 0 (fresh oil), 8, 50, and 94 h (Table 3). The corresponding oxidation provides evidence of the oil sample's degradation.

Table 3. Oxidation levels obtained by Fourier transform infrared spectroscopy (FTIR) [29] versus alteration duration of the engine oil. The samples for tribological testing were taken at 0, 8, 50, and 94 h [22]. An oxidation value of 12 indicates a severely deteriorated engine oil referring to the end of the oil's life span.

Alteration Duration in h	Oxidation in cm^{-1}
0	0
8	1.32
50	6.64
94	11.98

2.4. Tribometer and Test Execution

The selected tribometer was a linear oscillating tribometer (SRV4[®]). The tribometer testing parameters (Table 4) were selected on the basis of [22], where the influence of sliding velocity and temperature were investigated with the same tribometer and tribocontact set-up. For the present study with altered engine oil, the tribometer test parameters needed to be reduced with respect to the diversity of possible testing conditions and the available resources. Nevertheless, the selected test parameters represented boundary conditions occurring at the top dead centre of the tribocontact piston ring against the cylinder liner of a passenger car engine [26], and most of the piston ring–cylinder liner wear is expected to occur at the top dead centre position. Thus, the anti-wear additives of an engine oil need to work exactly at these conditions. At the same time, hydrodynamic and viscosity effects are reduced.

Table 4. Tribometer test parameters applied for the piston ring–cylinder liner setup in the SRV reciprocating tribometer based on the research of [22].

Load, in N	200
Frequency, in Hz	6
Stroke, in mm	3
Test duration, in h	25
Oil temperature, in °C	20 and 120
Inclination of the SRV chamber	90° (vertical contact)

On the other hand, the selected loading parameters for testing in the tribometer represent a regime of very conflicting trends of wear and tribofilm formation [22]. The higher temperature was expected to decrease the viscosity and thus lead to an increase in wear. Surprisingly, the opposite was found and correlated to the enhanced tribofilm formation with increased temperature. Thus, we focused on exactly these boundary conditions for investigating the impact of alteration of the engine oil.

The 20 °C temperature was aimed at simulating the sliding conditions in the boundary lubrication regime at the TDC during the cold start of the engine, while the 120 °C temperature emulated the sliding conditions near the TDC during the usual operating regime of the engine. Table 5 shows the number of tests performed with each temperature and oil ageing duration.

Table 5. Number of tests at 20 and 120 °C oil temperatures, conducted with fresh oil and the differently aged oils.

	Fresh Oil	8 h Aged Oil	50 h Aged Oil	94 h Aged Oil
20 °C	2 tests	2 tests	3 tests	2 tests
120 °C	2 tests	3 tests	2 tests	2 tests

Prior to tribological testing, the samples were cleaned in an ultrasonic bath with petroleum ether for 30 min. After the tribological tests, samples were rinsed in the petroleum ether to remove the residual lubricant.

A closed fluid circuit was attached to the sample holder and supplied the tribological contact with lubricant. The sample holders were surrounded by a rubber below. This enclosure prevented oil loss, which was especially important as the SRV chamber was inclined to 90° , meaning that the tribocontact was oriented in the vertical direction to allow wear particles to flow off easily. The outlet of the enclosure/triobocontact was connected to the gamma radiation detector via the closed circuit. The wear particles containing the radioactive Co57 tracer isotopes were transported to the detector by a fluid pump, with the lubricant circulating in the closed loop. Wear volume and depth were determined continuously throughout the test from the measured activity of the wear particles (also refer to Section 2.6). As supporting information, the friction coefficient was recorded during the test by an inbuilt sensor of the SRV4[®] test rig.

2.5. Surface Analysis (XPS)

The focus of the surface analyses was laid on the cylinder liner pieces, as also the wear measurement with the radioisotopes was performed with the cylinder liner pieces.

XPS analyses were performed on a Thermo Fisher Scientific Thetaprobe with a monochromatic Al K α X-ray source (1486.6 eV). High-resolution elemental spectra were acquired at a pass energy of 50 eV. Evaluation by Gaussian/Lorentzian peak fitting was conducted using the Thermo Fisher Scientific Avantage Data System software. The C1s peak for adventitious carbon at 284.6 eV was used as binding energy reference. Sputter depth profiles were acquired using 3 keV Ar ions, with a sputtering rate in the order of 0.2 nm/s. For the purpose of exhibiting the XPS data, pure element concentration was utilised for the P, Ca, and Zn elements, without differentiation between their various chemical states. However, the chemical states of sulphur were an exception. In this case, binding energy of 162.5 eV was allocated to the sulphides, and binding energy of 169 eV was assigned to the sulphate.

2.6. Wear Measurement

Since very low wear rates were expected for the investigated tribocontact lubricated with additivated engine oil, the radio isotope concentration (RIC) method was applied [29], as this technique allows wear measurement with high resolution in the range of nanometres per hour. The RIC method is based on the use of radioactive tracer isotopes and thin layer activation (TLA). The fundamental working principle is described in [30]. These isotopes were produced prior to the test in a separate activation process in a thin surface layer of a few micrometres of the cylinder liner specimens. The concentration of the tracer isotopes in the material of the activated zone was determined for each activation. These so-called activated components were installed in the tribometer for the purpose of the wear measurement. For the RIC method, a gamma radiation detector was connected to the closed fluid circuit, which supplied the tribocontact with lubricant. The wear particles were carried by the lubricant to the radiation detector, where the activity of the isotopes was measured. With the knowledge about the concentration of the tracer isotopes originating from the specimens' wear zone, the wear volume or the average wear depth was determined. The latter can be derived from the wear volume when the area of the wear scar is known.

The RIC enabled measuring the wear continuously throughout the test run with the determination of a wear curve depicting the change in the wear over time. Commonly, the wear behaviour of lubricated components can be described by two phases: the running-in wear phase occurring right after the start of operation or after changes in the operating conditions, and the steady-state wear regime after the running-in wear is phasing out and the surfaces of the tribocontact are adapting to steady-state conditions. To compare the wear behaviour quantitatively, the steady-state wear rate (w_s) was calculated by fitting the wear curve with a linear function using the least square method in the steady-state wear regime. In the present results, the last 40% of the test duration was set as the steady-state regime for the linear fitting (Figure 2).

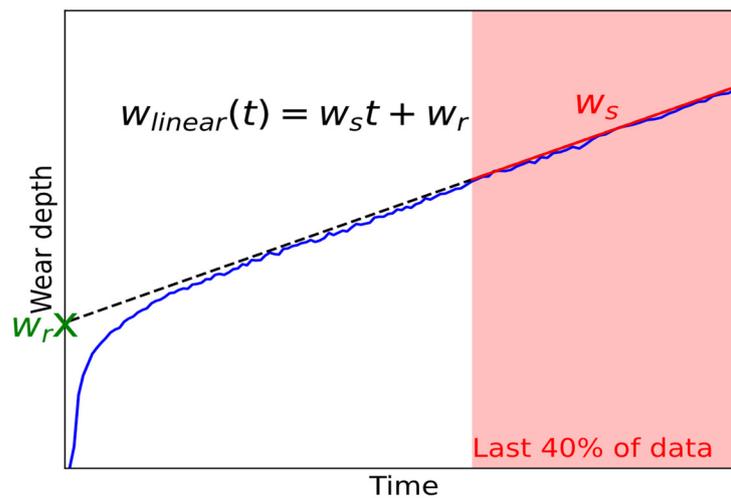


Figure 2. Visualization of the definition used for wear curve evaluation. The steady-state wear rate (w_s) is calculated by fitting the last 40% of wear depth data, while the running-in wear (w_r) is defined as the value of interception of the y -axis with the extrapolated fit w_s .

This definition seems to be reasonable according to the trend of most observed wear curves and the chosen test durations. The running-in wear (w_r) was subsequently defined as the Y -axis intercept of the linear fit at the X -axis value of zero (equal to the starting time of the test).

3. Results

3.1. Wear and COF

Figure 3 shows the coefficient of friction over time for different oil alteration states and oil temperatures of 20 and 120 °C. CoF data were retrieved from the SRV4[®] tribometer, calculated from the highest values of the measured friction force (approximately the top 10%), and additionally averaged over several strokes. Consequently, the obtained COF values were related mainly to the relatively high friction forces at the turning points of a stroke, where low relative velocities implicate a reduction of the lubricating film. The COF values obtained by the applied set-up were related to a lesser degree to the moderate friction forces at the mid-stroke region of an engine stroke, where hydrodynamic effects are dominating. With the frequency of 6 Hz and the stroke of 3 mm, the sliding velocities were so low that the values of coefficient of friction were mostly determined by solid–solid contact and such by boundary and mixed lubrication conditions. Hydrodynamic conditions were not expected to occur within these settings.

Small fluctuations in the running-in phase of all CoF curves in the range of 1 to 3 h were followed by stable behaviour during the rest of the experiments. In general, the given CoFs after the running-in phase were settled in a very tight range between 0.15 and 0.18. Hence, a correlation between the coefficient of friction and the oil ageing duration or the oil temperature was not evident from the measurement data.

In Figure 4, wear curves of cylinder liners are shown for measurements performed with fresh, 8 h altered, 50 h altered, and 94 h altered oils using test temperatures of 20 °C and 120 °C. Two measurements with 50 h altered oil and 20 °C were interrupted by unintentional stoppage of the fluid pump (Figure 4c). The time of stoppage is marked with an *, and the data for evaluation were only considered until this point for those two measurements, because after the restart of the pump, the wear depth level was slightly elevated. The tests until the * were considered valid by the authors, since the wear curve was obviously already in the steady-state wear regime, and no further change in wear behaviour was expected.

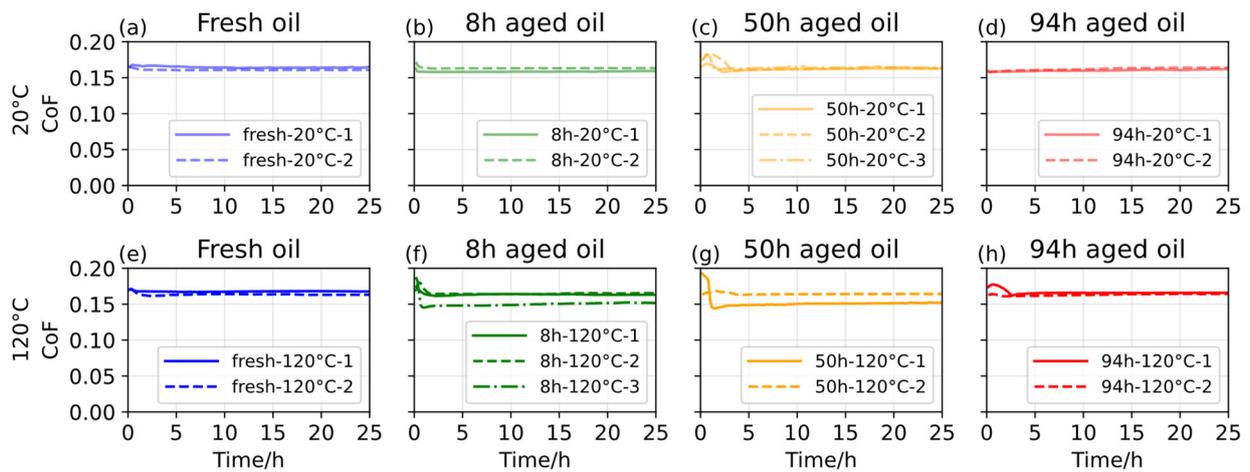


Figure 3. Coefficients of friction (CoF) measured at 20 °C ((a–d), top row) and 120 °C ((e–h), bottom row) oil temperature, performed with oils with different alteration status.

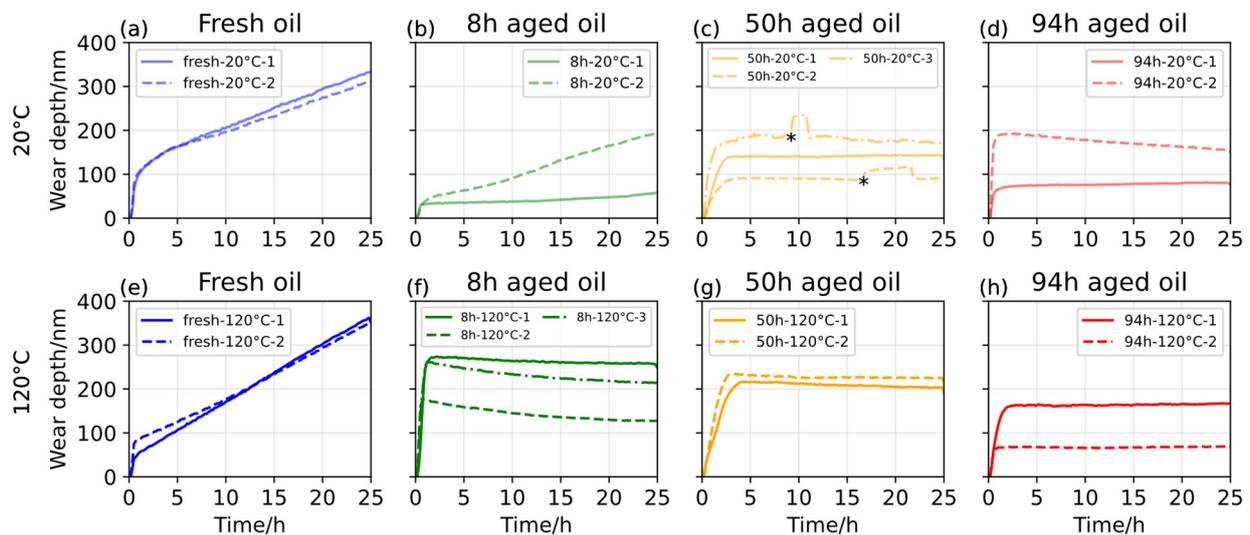


Figure 4. Wear depth of cylinder liner samples at 20 (a–d) and 120 °C (e–h) test temperature using fresh, 8 h, 50 h, and 94 h altered oils. Measurements marked with * were only evaluated until this point in time (due to pump failure).

The wear curves were evaluated by determining the running-in wear and the steady-state wear rate following the definitions described in Section 2.6. For the measurements with identical conditions (in terms of oil temperature and ageing duration), the running-in (Figure 5a) and steady-state values (Figure 5b) were averaged. The black bars represent the minimum and maximum values of the corresponding wear parameters.

Running-in behaviour (Figure 5a): A reliable interpretation of the running-in behaviour would need a higher number of statistics, as running-in is explicitly affected by starting conditions, which include local effects like pores or dust particles. Nevertheless, a rough trend could be observed, as the running-in with the fresh oils was somewhat lower than the running-in with the altered oils. The low running-in values from the tests with 8 h alteration and 20 °C may be explained as a kind of transition stage between fresh and altered condition, as also observable by the diversity of steady-state wear rates, see Figure 5b.

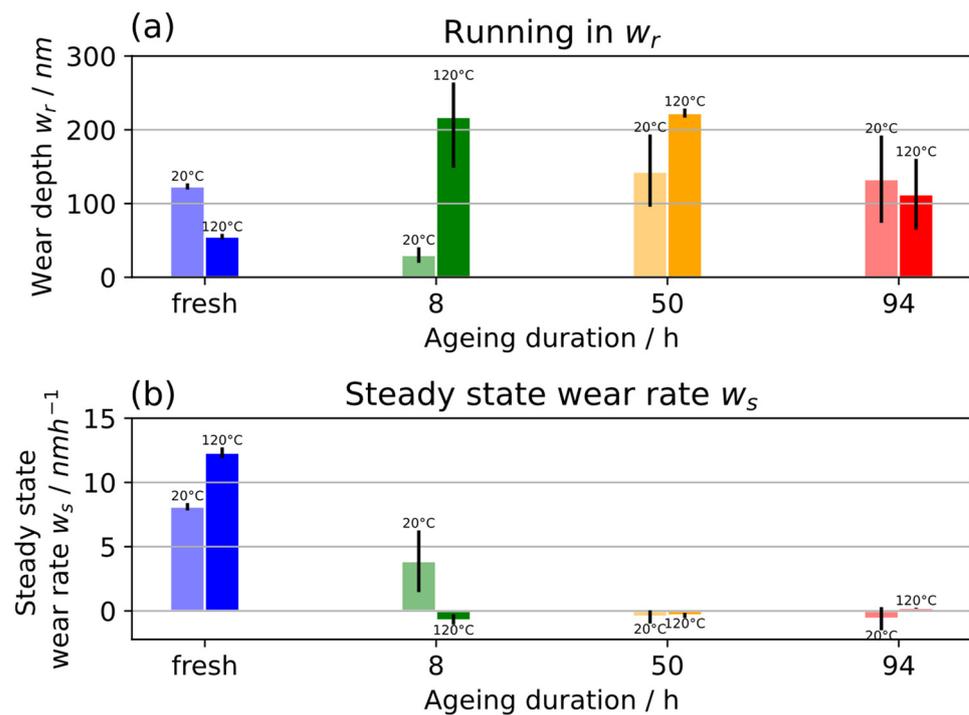


Figure 5. Comparison of running-in wear (a) and steady-state wear rates (b) of cylinder liner using oil with different altered states (fresh, 8 h, 50 h, and 94 h alteration) and test temperatures of 20 and 120 °C. The black bars show the range between the minimum and maximum values.

Steady-state wear rates (Figure 5b): For the steady-state wear rates, the change in wearing behaviour with advanced alteration was significant, despite the limited statistics within this study. For fresh oils, the steady-state wear rate was by far higher than that for the tests with altered engine oils. Only the condition with 8 h altered oil and 20 °C was somewhere between the fresh condition and the series of altered conditions, as already implied before in the running-in interpretation. Two effects may lead to that behaviour. Firstly, 8 h alteration seemed to produce engine oil in which the decisive component was not completely converted. This is in accordance with the findings of Dörr et al. [17], outlining intermediates such as dihexyl thiophosphate as one of the degradation products of dihexyl dithiophosphate (DDP) of the ZDDP alteration, with a clear occurrence with alteration duration. Secondly, an increased temperature during the tribotests seemed to be another trigger, either to complete the alteration or at least to emphasize the reaction of the already converted species at the surfaces of the tribocontact.

Nevertheless, the wear measured by the RIC method detected the wear of the initially activated substrate and was not (in this kind of set-up) capable of detecting the wear of the tribofilm. The wear quantification and, consequently, the negative wear rates are discussed in detail in Section 4. Before that, the build-up of the tribofilm needs to be understood, and the corresponding tribofilm analysis is described in the next section.

3.2. Elemental Analysis of Tribofilm

For clarifying the impact of the altered engine oils, a tribofilm analysis via XPS is the most respected and widely used analysis technique, especially when focussing on investigating the thickness and chemical composition of the tribofilm [10,31,32]. Unfortunately, the samples with 8 h alteration state and 20 °C test temperature were not available for XPS analysis. Nevertheless, the specimens with 120 °C test temperature were regarded to be a representative group for analysing the alteration impact. Within the XPS analysis, the focus is laid in the following section (Figure 6) on the components of ZDDP, namely Zn, S, and P, as well as on Ca as the representative of detergents. The XPS data were evaluated according to the method described Section 2.5. In Section 4.4, additional information is

given for the elements C and Fe, with a specific elemental state of iron as iron-oxide and bulk iron.

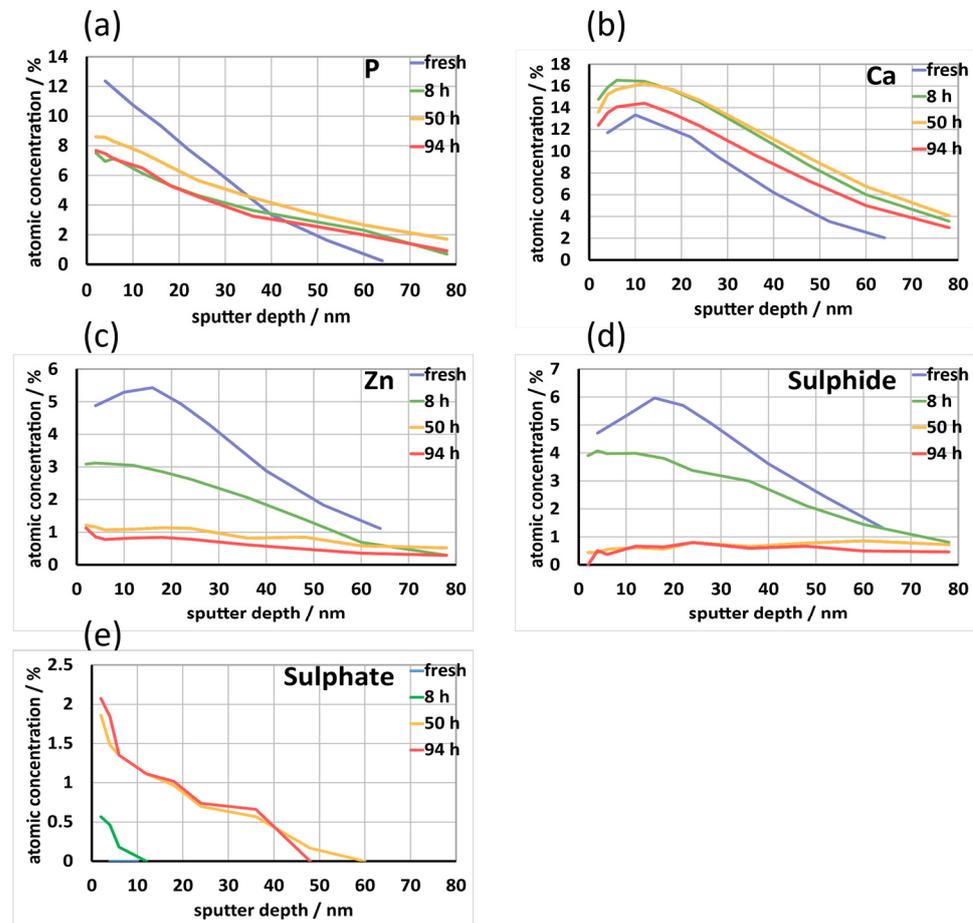


Figure 6. Distribution of P (a), Ca (b), Zn (c), sulphide (d), and sulphate (e) in atomic percent over sputter depth in nm for tribofilms with different ageing status of lubricant.

Figure 6a,b show the distribution of phosphorus (P) and calcium (Ca), respectively. These two elements are regarded to form short- and long-chain calcium-phosphates, even leading to a glass-like condition of the tribofilms [6,33–35]. For P, a drift in elemental concentration could be observed, changing from a relative concentration at the very top surface for the fresh engine oil condition to a broader distribution in depth for the altered states of the engine oils. For Ca, which is a representative element for detergents present in the fully formulated engine oil, an increase with altered status was evident. Surprisingly, the trends for P and Ca were not perfectly parallel, indicating a shifting of the molecular forms considering P and Ca.

As the tribofilm formation is strongly correlated with ZDDP, the distribution of Zn is another essential piece of information. Comparing the Zn distribution (Figure 6c) with the sulphide state of S (Figure 6d), a convincing conformance could be observed in the form of the distributions as well as in atomic concentration. Thus, ZnS was present in the top layer of the surface (10–20 nm) for the fresh oil condition in the range of 5 to 6% and decreased with the altered oil conditions, down to roughly 1% for the strongly altered oils.

A completely different behaviour was found for S in the sulphate state, which was practically not present in the tribofilm with the fresh oil condition but increased with increasing altered state (Figure 6e). It must be remarked that S in the sulphide state was present in the tribofilm of the fresh oil condition up to 6%, whereas S in the sulphate state did not exceed 2%. Nevertheless, the ratio of sulphide to sulphate tilted.

As the tribofilm with fresh condition and 120 °C hardly contained any sulphate (refer to “fresh” in Figure 6e), the test temperature and the impact of shear due to sliding were inadequate for sufficiently enabling the reaction of sulphide to sulphate. Obviously, the alteration process due to temperature and oxidation was needed to provide the sulphate form to build up such a tribofilm. The prominent literature about the molecular processes of ZDDP indicates phosphorus as the dominant factor [36,37] (see also Section 4.3). As the phosphorus distribution in the tribofilms (Figure 6a) did not change significantly, P was regarded as not being the driving factor for the dramatic change in the wearing behaviour. Instead, the sulphate increase, that moved in parallel to the sulphide decrease, showed a remarkable correlation with the changes in the wear behaviour, when changing from fresh to altered engine oil (compare Figure 6e with Figure 5b). As both measurement methods, the wear measurement and the elemental tribofilm analysis, are regarded to be reliable and reproducible, the correlation of a lower wear rate with a higher sulphate ratio is regarded as a strong indication and a remarkable finding.

This could already be the end of the story, as there was a clear correlation between the reduction in the steady-state wear rate with increased sulphate content in the tribofilm compared to the fresh condition. Surprisingly, the continuously measured wear signals (Figure 5b) revealed wear rates even going negative in the assumed steady-state conditions. This phenomenon needs to be analysed in detail before drawing conclusions about wear behaviour and tribofilm impact with altered oil conditions.

4. Analysis of Negative Wear Rates and Discussion

4.1. From Running-In to Steady-State Wear

The wear results for the cylinder liners tested with altered oils occasionally showed the phenomenon of a decreasing wear signal in the steady-state regime, which would indicate negative wear rates and thus a peculiar result (Figure 4b). In the case of the RIC measurement technique, it meant that the number of wear particles or wear volume in the lubricant was decreasing with time (or in simplified terms, fewer particles were detected by the detector in the lubricant). The most obvious explanation for the decreasing wear signal was a continuous removal of wear particles from the closed loop. Removal could arise from leakage of the lubrication circuit or particle traps in the lubrication circuit. Loss of lubrication could be excluded by measurement of the lubricant volume before and after the test. The loss of particles in the circuit (e.g., sedimentation or deposition on tube walls) was investigated by pumping a defined amount of activated wear particles through the lubricant circuit without an active wear or friction process—meaning with the SRV4[®] reciprocating movement being stopped. The signal emitted by the activated wear particles was measured continuously for 25 h.

This measurement (black line in Figure 7) showed a marginally decreasing wear signal with a calculated “wear rate” of $w_o = -0.03$ nm/h. This was a representative indicator for a “zero” line with hardly any particles trapped or deposited in the lubrication circuit on tube walls and circuit encapsulation. This was ascertained by measurements of the tubes and circuit components after the experiments, showing a maximum activity of less than 1% of the total wear activity (which did not significantly differ from the omnipresent background for radioactive measurements) being deposited in the lubricant circuit.

Additionally, the total wear activity was checked by comparison of the activity of the activated and cleaned specimen before and after the tribological experiment. This direct measurement of the activated specimen was subject to a higher uncertainty than the indirect measurement of the wear by means of the wear particles in the circuit due to the statistical limitations when comparing large values. Thus, the direct measurement of the specimen confirmed the correctness of the magnitude of the RIC measurement but was not able to assess the depths of the wear process. Summarising the two statements above, the loss of the specimen due to wear was confirmed by the direct measurement, which correlated with the volume of wear particles, and additionally, hardly any particles were lost in the lubricant circuit when there was no tribological action.

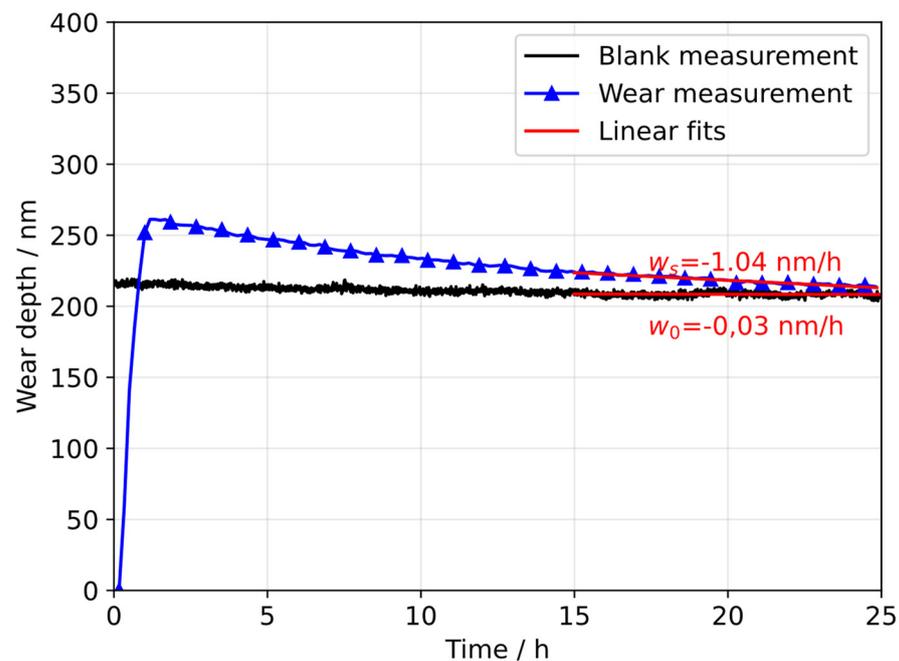


Figure 7. Comparison of wear particle losses during continuous flow in the lubricant circuit with disabled tribocontact (black line) and enabled tribocontact (blue line with triangle markers). w_s indicates the loss of wear particles during an active tribocontact in comparison to w_o , which serves as the reference for particle losses at tubes and circuit components with disabled tribocontact.

However, a representative wear measurement with altered oil condition (blue line with triangles in Figure 7), where the reciprocating movement of the SRV4[®] tribometer, and thus the wear process, was in progress, revealed a significant decrease in the wear signal in the assumed steady-state condition. It became apparent that the absolute value of the negative “wear rate” ($w_s = -1.04$ nm/h) was magnitudes higher than the rate w_o of the blank measurement with disabled tribocontact.

Comparing the measurement with disabled tribocontact and the corresponding wear measurement with active tribocontact, it can be concluded that the negative wear rates in the wear measurement could hardly be explained by particle losses in the lubricant circuit on tube and chamber walls. Therefore, the authors suggest the hypothesis that wear particles are incorporated from the flow of lubricant into the tribological contact during tribological loading. The incorporation of wear particles can also occur in wear measurements with positive wear rates (e.g., Figure 4a,e) but are less apparent due to the superposition with the signal of newly produced wear particles from the initially activated specimen. Thus, wear must be seen as a manifold process, at least including the wear of the initial specimen, which is the classical understanding of wear in the sense of (abrasive) loss of material, the wear of the tribofilm, and the incorporation of the wear particles into the tribofilm.

4.2. Approach for Quantification of “Incorporation of Wear Particles” Due to Decrease in Wear Signal

Based on the model picture that the wear particles are incorporated in the tribolayer during the formation of the tribo-layer from constituents of the lubricant, the wear measurement is an indirect signal for the formation and wear rate of a tribofilm. This gives us the opportunity to approach this phenomenon metrologically and to enable a measurement-based quantification. The wear signal is the result of three main processes, outlined above—the wear of the initial specimen, the wear of the tribofilm, and the incorporation of the wear particles into the tribofilm. Nevertheless, an estimation of the minimum incorporation rate can be achieved.

Figure 8 shows an exemplary wear curve, which is used to illustrate the quantification method. In a wear curve, the particle concentration reduction manifests in the decrease in wear depth signal (Δw) in the oil measured by the RIC method. $y(t_i)$ describes the wear depth values at time t_i (of the data of the wear curve measured by the RIC method), and w_{linear} is the function of the determined linear fit analogous to the method described in Figure 2.

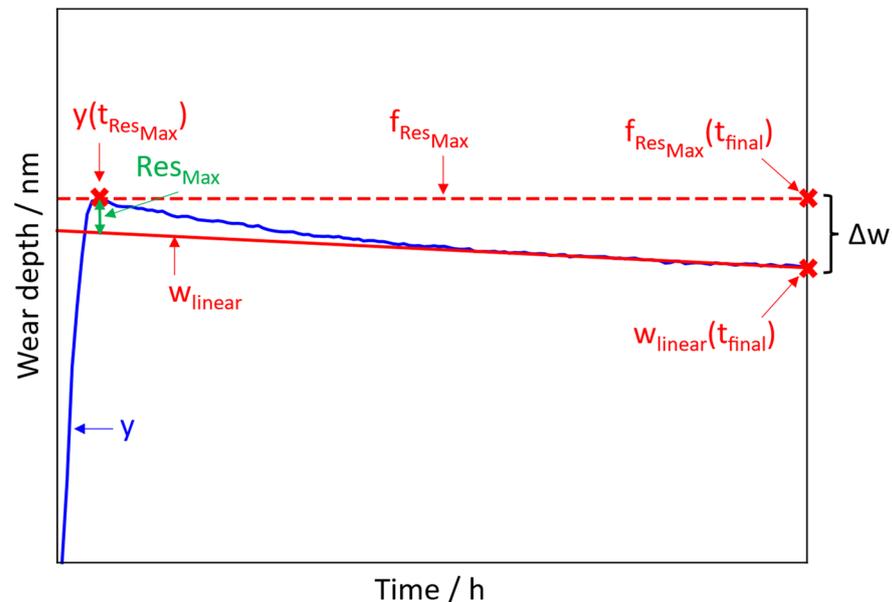


Figure 8. Quantification approach of particle reduction in lubricant.

Then, the maximum residual of y and w_{linear} is obtained through:

$$Res_{Max} = \max(y(t_i) - w(t_i)_{linear}) \quad (1)$$

Then, t_{ResMax} represents the corresponding time of Res_{Max} .

Hence, the function value at t_{ResMax} on the wear curve y is $y(t_{ResMax})$, which is consequently a minimum estimate of the running-in wear. In some publications, the running-in is associated with reducing the roughness tips as well as with the geometrical adaption of the counteracting surfaces [38,39]. Regarding the findings described in Section 3.2, we consider the formation of a tribofilm a similarly important running-in mechanism, at least for lubricated tribocontacts. The building-up of a tribofilm will reduce the wear of the substrate underneath the tribofilm due to its protective nature. Thus, the running-in wear will asymptotically follow an exponential curve to a value, which would then give the uninfluenced, maximum running-in value. At the same time (or with a slight delay proportional to the building-up of the tribo-film and production of the wear particles), the incorporation of the particles into the tribofilm will occur. This process can as well be interpreted as an exponential decay due to the statistical probability of different related processes.

If these two exponential processes together with the linear, steady-state wear rate need to be mathematically fit to the measurement signal, there will be numerous, mathematically equivalent outcomes that contain no further information than the linear approach used in this study so far. For the exponential approach to be dependable, the exponential parameters need to be deduced by physical principles, which is outside the scope of this paper.

Continuing the estimation for particle incorporation, a linear function $f(t)_{ResMax}$ was defined for estimating the minimum wear of the initially activated specimen (refer to

Figure 8 dashed lines), which intersects the data point $y(t_{ResMax})$ at t_{ResMax} with the slope k_{ResMax}

$$f(t)_{ResMax} = k_{ResMax}t + d_{ResMax} \quad (2)$$

with a slope:

$$k_{ResMax} = \begin{cases} 0, & w_s < 0 \\ w_s, & w_s \geq 0 \end{cases} \quad (3)$$

and the offset at $t = 0$.

$$d_{ResMax} = y(t_{ResMax}) - k_{ResMax}t_{ResMax} \quad (4)$$

w_s is the steady-state wear rate for the last 40% of the test duration (see Figure 2).

$k_{ResMax} = 0$ for $w_s < 0$ considers that there is no plausible reason why the wear of the substrate should become negative, as well as that we proved that no (noteworthy) particles are lost in the lubricant circuit elsewhere. Thus, (3) gives the minimum wear rate of the initially activated substrate.

Finally, the incorporation of wear particles into the tribofilm is considered as the difference between the wear of the substrate $f(t)_{ResMax}$ and the measured wear signal $y(t)$ at the test end t_{final} :

$$\Delta w = f_{ResMax}(t_{final}) - y(t_{final}) \quad (5)$$

This quantification method allows for a consistent evaluation of particle concentration reduction for all wear curves. This approach also allows for quantifying the particle incorporation for different shapes of wear depth curves (compare to Figure 4).

4.3. Particle Incorporation in Comparison to Altered Condition of Lubricants

Wear particles play a key role regarding the wear mechanisms of the piston ring and cylinder liner contact or of combustion engines in general. If the wear particle diameter exceeds the thickness of the lubricant film in certain operating conditions, the particles can act as abrasives on the component surfaces [40]. Srivastava et al. [41] also discuss the possibility of wear particles becoming embedded into one of the surfaces of the tribological contact, where they may cause grooves in the counteracting component, resulting eventually in progressive loss of material. This could be more likely for used oils, due to a higher concentration of wear particles after a long operating time. According to Popov et al. [36] the size of wear particles in modern engines varies from several nanometres to the micrometre range, with the highest fraction between 10 and 120 nm, with 50% of them being smaller than 40 nm. They also discuss the mechanism whereby wear particles are integrated again into the surface right after their generation, as they remain for a relatively long time in the friction zone.

Some studies discuss the incorporation of iron oxide wear particles into the tribofilm. Martin [37] describes the digestion of abrasive iron oxide particles into a zinc phosphate glass due to tribochemical reactions. Another study [42] used molecular dynamics (MD) simulations to investigate zinc metathiosphosphate and zinc metaphosphate for a better understanding of the ZDDP and ZP wear prevention mechanism. The simulations point out that the digestion of Fe_2O_3 wear particles is initiated by the shear-induced phase transition of ZDDP tribofilms. Moreover, they found that both $Zn(PS_{0.5}O_{2.5})_2$ and $Zn(PO_3)_2$ effectively incorporated Fe_2O_3 particles during friction, contributing to the wear preventing mechanisms of ZDDP. Berkani et al. [43] investigated the depolymerization of zinc metaphosphate (which is an important reaction in the ZDDP tribofilm formation) with respect to the tribofilm generation on steel and the digestion of particles in the film. By adding specific types of particles (Fe_2O_3 , Fe_3O_4 , FeO , $FeOOH$), they found that only $FeOOH$ particles lead to a reaction between the particle material and zinc metaphosphate, which results in a full depolymerization of the polyphosphate in a tribo-stressed situation with

both shear and pressure. Such reactions are known to take place at the top of the native oxide layer on steel surfaces.

With the method described in Section 4.2, the minimum wear rates as well as the minimum amount, Δw , of incorporation of wear particles can be deduced and displayed over the altered status of the lubricant (Figure 9).

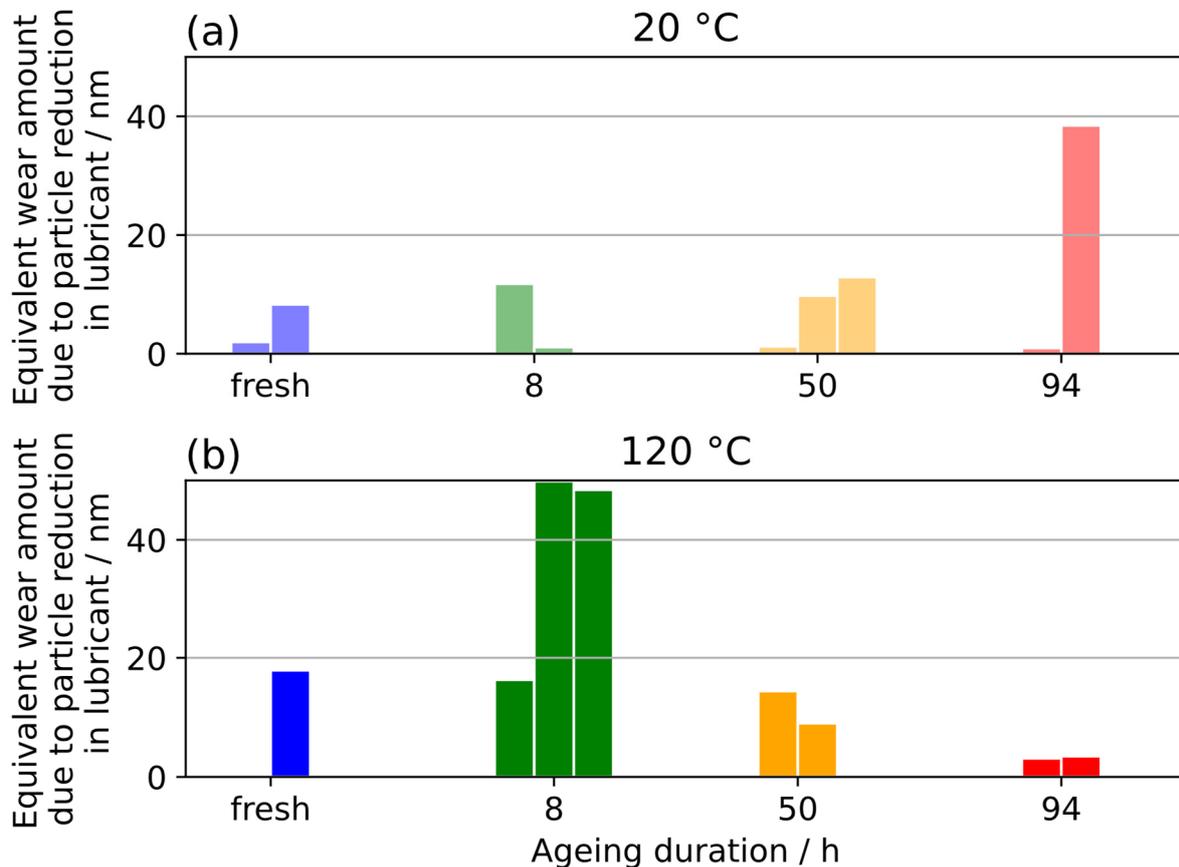


Figure 9. Equivalent wear amount due to reduced particle concentration in the lubricant circuit at 20 °C (a) and at 120 °C (b) oil temperature.

For the 20 °C test temperature (Figure 9a), the incorporation was less pronounced than for the 120 °C test temperature (Figure 9b). Here, the higher test temperature seemed to have an intensifying effect on the ability of the tribofilm to reincorporate wear particles. Further, at the 20 °C test temperature, the ability of incorporation was likely similar for the different altered conditions, whereas at 120 °C, there was a clear peak at the 8 h altered condition. Carefully said, there was also a trend at 120 °C in which the ability of incorporating particles vanished with increased altered status.

For the sake of curiosity, we would like also to document an observation that might give a hint for a possible further explanation. When carefully considering the wear progress, for some experiments with the 20 °C test temperature and with fresh and 8 h altered status as well as for the 120 °C test temperature and 94 h altered status, a kind of sagging in the wear curve could be observed (Figure 4b,h). This may indicate that an amount of the wear particles incorporated in the tribofilm was released again to some extent. This may have been due to increased wear of the tribofilm or due to a reduced ability of the tribofilm to regenerate and to incorporate wear particles. For the fresh and 8 h altered conditions, this may have been because the alteration did not generate enough species that form the tribofilm or that cover the wear particles to glue them onto the surface. Let us assume that this might be due to the lack of sulphate species. A similar effect may be true for the test

condition at 120 °C with the 94 h altered status, but due to exhausting the available species in the lubricant to incorporate the wear particles.

In the works of Spiller et al. [23] and Miranda-Medina et al. [25], the effect of changing from fully formulated engine oil to non-additivated PAO8 was investigated. There, the existing tribofilms from the fully formulated oils turned into carbon-rich tribofilms when running with non-additivated oils. These carbon-rich tribofilms were also found in the present work on the sample surfaces tested with the aged oils, but not for the fresh oil variant (see Figure 10a–d). The increase in the amount of carbon on the surface paralleled the increasing oil alteration time, and thus the oxidation level of the lubricant. The oxidation of lubricant substances leads to the generation of acidic products in the oil, which could result in iron oxides in the wear particles or the surface. Remarkably, these carbon-rich tribofilms can efficiently protect the specimen underneath and as such, provide low steady-state wear rates. With this finding in mind, a look at the increasing content of carbon in the tribofilm with increased alteration and, hence, oxidation value of the lubricant leads to a model whereby carbon species overtake the role of the components of the ZDDP additive in the tribofilm formation, but through that, the ability of the tribofilm to incorporate or embed wear particles is reduced. Thus, this incorporation is somehow linked to the presence of a certain sulphate species that is produced through the alteration of the lubricant (refer to Section 3.2) but likely reduced or even completely degraded through further alteration.

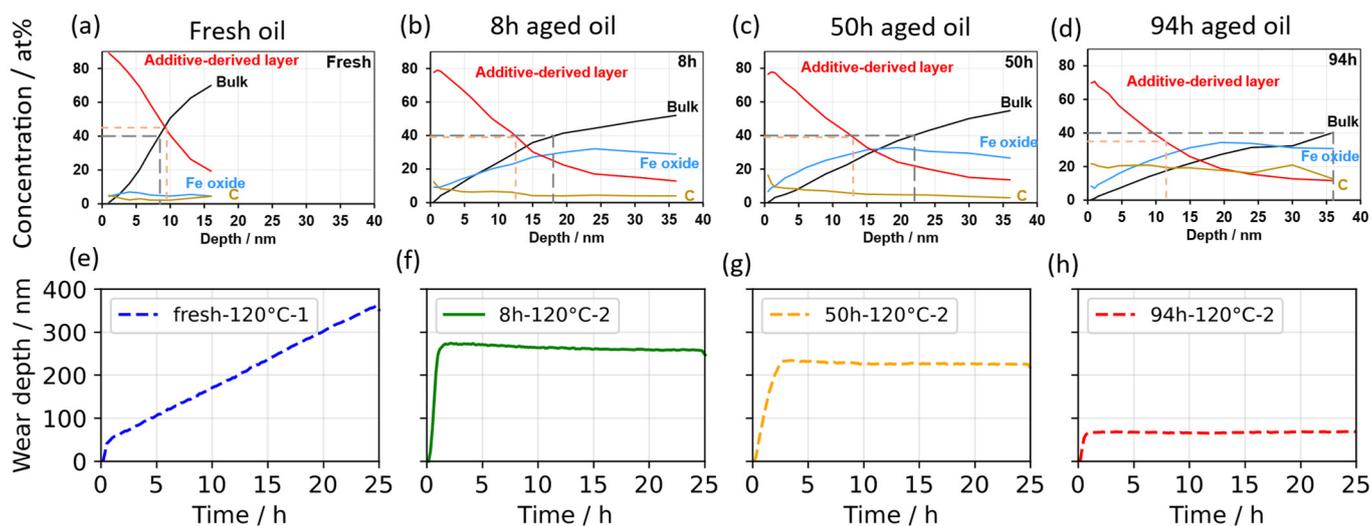


Figure 10. Comparison of XPS sputter depth profiles of the tribefilm samples (from measurements with fresh, 8 h, 50 h and 94 h aged oil (a–d) at 120 °C test temperature) with the corresponding RIC wear curves (e–h).

Before we go too far into hypothesis, we would like to come back to reproducible analyses. If the idea of incorporation of wear particles is true, we need to find them in the tribefilm.

4.4. Iron-Oxide as Part of the Tribefilm

Considering the literature, the ability of a tribefilm to prevent or reduce wear is always connected to the term “tribefilm thickness”. There are different definitions available for tribefilm thickness, such as the reduction of the concentration of lubricant additive components to half of their top surface concentration. In the present study, we preferred to use the concentration of the bulk iron for estimating the tribefilm thickness. As such, the tribefilm thickness is the distance to the surface when the bulk iron concentration reaches half of its bulk value and so 40% of the absolute atomic concentration.

With this definition of the tribefilm thickness, an increase in the thickness can be observed with altered conditions (grey dashed lines in Figure 10a–d). This would not be that clear if the concentration of the lubricant additive components had been taken

as the tribofilm thickness (indicated as “additive derived layer” in Figure 10a–d, dashed orange line).

In between the additive-derived layer and the bulk iron, there is a layer of iron oxides (blue line in Figure 10a–d). This iron-oxide layer was significantly pronounced for the experiments with altered oil conditions (Figure 10b–d) and obviously correlated with the significant reduction in steady-state wear rates (Figure 4b). Remarkably, the total amount of the iron oxides was of the same magnitude as that observed by the wear measurement for the minimum wear particle incorporation (Figure 10b). In detail, a concentration of roughly 30% over at least 30 nm (Figure 10b–d) estimated through the XPS depth profile (Figure 10b–d) corresponds to 100% of at least 10 nm, which is in some kind of agreement in order of magnitude with the wear particle incorporation estimated through the RIC measurement (Figure 9b). Thus, the iron-oxide layer is mainly formed by the initial wear particles that have been incorporated into the tribofilm. This is in accordance with the findings of Miranda-Medina [25], who analysed very similar tribofilms via TEM and EDX. In these tribofilms, iron oxides were found as part of the tribofilm and, through the inhomogeneous distribution of the iron oxides, it could be concluded that an embedding of particles into the tribofilm had occurred.

Based on these findings, some kind of corrosive reaction, e.g., of the sulphate species with the bulk iron to form an iron-oxide layer underneath the additive derived tribofilm, cannot be excluded and may be an additional effect. Nevertheless, the incorporation of the wear particles must be regarded to be a fact due to the principles and properties of the applied wear measurement method with radioisotopes as tracers.

5. Conclusions

Experiments conducted by means of an oscillating tribometer with piston ring against a cylinder liner model contact in boundary lubricating conditions revealed changes in wear behaviour with respect to different grades of altered engine oil. The alteration was performed through laboratory ageing at 180 °C and air flow, emphasising oxidation of the lubricant. The engine oil was fully formulated and, as such, ZDDP was a key factor for tribofilm formation and thus anti-wear effects. The applied wear measurement technique was based on radioisotope tracers and, as such, able to discriminate the changes in wear behaviour of the initially activated substrate with respect to the altered states of the lubricating oil.

- The steady-state wear rates in experiments with altered lubricants were significantly lower in comparison to those in experiments with fresh lubricants. This applied for both test temperatures, 20 °C as well as 120 °C. This is against the common expectation that aged oil should lead to a higher wear rate compared to the fresh oil condition.
- Based on XPS analysis of the formed tribofilms at the 120 °C test temperature, the decrease in sulphide and increase in sulphate states with altered conditions became apparent and directly correlated with the decrease in steady-state wear rates with altered conditions of the lubricant. Thus, altered lubricants are better in building-up a wear-preventing tribofilm than lubricants in the fresh condition, and the sulphate species of the lubricant play a key role in the formation process.
- The XPS analysis as well showed the formation of an iron-oxide layer in between the additive-derived layer and the bulk iron. The amount of iron oxide was of an order of magnitude comparable to that observed by the wear measurement method for the loss of wear particles. Through complementary measurements, a loss of wear particles in the lubricant circuit due to leakage or deposition on tube walls could be neglected. Thus, the wear particles were (re-)incorporated from the lubricant and flowed into the tribofilm.
- Through analysis of the wear curves, estimates of the minimum amount of incorporated particles could be deduced, considering the complementary processes of wear of the initial surface as well as wear of the tribofilm itself. Nevertheless, the effect of incorporating wear particles into the tribofilm was strongest for the lubricant

condition with 8 h ageing. Based on the comparison of the steady-state wear rate and tribofilm composition, the lubricant condition of 8 h ageing is considered to be an intermediate state between the fresh and fully aged condition. Through comparison with [17], this correlates with dihexyl thiophosphate, the intermediate product in the decomposition of ZDDP.

Further research could focus on the role of sulphate and its molecular involvement in the formation of the tribofilms as well as on the understanding of the wear behaviour of the sulphate-induced tribofilm itself. Currently, it is not yet clear whether the tribofilm prevents wear at all or if the tribofilm itself wears instead of the underlying substrate. Further to the wear of the tribofilm, the complexity of the constant rebuilding of the tribofilm in relation to the availability of additives or altered products of the additives as well as the presence and incorporation of (wear) particles is not fully understood.

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