

Article

Impact of Soot on Internal Combustion Engine Lubrication—Oil Condition Monitoring, Tribological Properties, and Surface Chemistry

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Abstract: In the study at hand, a systemic investigation regarding the tribochemical effects of crankcase soot is presented. Sooted oils were generated via an engine dynamometer test. Both conventional as well as advanced oil condition monitoring methods indicated a mild degradation of additives. The wear volume was greatly increased with the sooted oils in model tribometer tests, despite the high residual zinc dialkyl dithiophosphate (ZDDP) antiwear (AW) levels. Once the soot was removed via ultracentrifugation, the wear volume returned to levels comparable to the fresh oil. Surface investigations revealed that ZDDP tribofilms could not form in the sooted oils, as only a thin sulfide layer was present on the metal surfaces. Meanwhile, typical tribofilms were observable with centrifuged oils. The results indicated that a tribocorrosive mechanism is most likely responsible for the elevated wear in the sooted oils, where only the iron sulfide base layer of ZDDP films is formed, which is then rapidly removed by the soot particles in an abrasive manner.

Keywords: soot; oil degradation; internal combustion engine; diesel engine; wear; antiwear additive; zinc dialkyl dithiophosphate (ZDDP); high-resolution mass spectrometry; tribofilm; X-Ray photoelectron spectroscopy (XPS)



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1. Introduction

Environmental aspects, especially the need for a reduction in carbon dioxide (CO₂) emissions, will be one of the major challenges in the transportation sector within the next years. Compression ignition (CI or diesel) engines have a higher thermal efficiency by design compared to spark-ignition (SI or Otto) systems, as the compression ratio and turbocharging are restricted in SI engines [1]. Accordingly, CI engines offer a key advantage for the transportation sector, despite the challenges of NO_x and particulate matter (PM) emissions commonly associated with such systems. In 2022, CI engines had a market share of only 16.4% (over 180,000 vehicles) in the passenger fleet [2], but they had a market share of 96.6% among the new freight vehicles in the EU [3], corresponding to over 270,000 individual units. Additionally, the market share of CI was over 70% in the maritime shipping industry globally [4]. This shows that CI is primarily a technology for fuel consumption-sensitive areas, such as on-road freight transport or maritime shipping, mainly due to its better thermal efficiency and, as such, lower CO₂ emission and fuel costs. Since SI and battery electric (BE) drivetrains are impractical due to either lower thermal efficiency or insufficient energy density, it is expected that CI technology will remain available in such areas. Although there are alternative propulsion technologies available, they currently seem to be less suitable, e.g., for long-distance maritime shipping, a purely BE drivetrain is currently impossible, as the volume of the battery pack would exceed the total cargo capacity of most ships [5]. Nevertheless, environmentally friendly operation is one of the key goals in the mobility sector, where CI drivetrains have some disadvantages, especially in the maritime industry. These disadvantages can be compensated for by the utilization of more sustainable fuels. One potential carbon-free alternative fuel for CI engines is

ammonia [5]; however, lubrication of ammonia-fueled engines can be challenging due to different chemical interactions and lubricant degradation [6]. Alternatively, hydrogen combustion can also be utilized to reduce carbon emissions; hence, it has been considered as a viable option [7]. Consequently, further development of CI powertrains for on-road and marine freight transport is expected, and the tribology and tribochemistry of CI engines still remain interesting topics. Accordingly, development of novel additives is also undertaken. For example, nanofluids might be a promising alternative. Zinc oxide (ZnO) and molybdenum disulfide (MoS₂) nanoparticles have positive effects on the tribological properties of diesel fuels, such as increased viscosity and reduced coefficient of friction in relatively low concentrations (0.4–0.7 m%) [8]. Graphene oxide (GO) nanoparticles doped with Cu, ZnO, and MoS₂ can also increase the fluid viscosity, viscosity index, and flash point, while simultaneously reducing friction and displaying antiwear properties [9].

1.1. Soot Formation and Properties

Soot formation and subsequent emission is characteristic for CI engines [10,11]. Field studies showed that in-service SI and CI engine oils differ significantly in this regard [12], which is sometimes correlated with higher wear rates observed in CI engines [12]. The origin of soot particles in CI engines is comprehensively presented in the review of Tree and Svensson [13] and is only briefly summarized below. Soot forms through a series of thermo-oxidative reactions. In detail, the following distinct processes are involved:

- Pyrolysis, the formation of polycyclic aromatic hydrocarbons (PAH) and acetylene precursor molecules at high temperature, largely without oxidation.
- Nucleation, the formation of 1.5–2 nm solid particles through the radical addition of aliphatic hydrocarbons on the precursors.
- Surface growth, the increase in particle mass through absorption of mostly acetylene from the gas phase—the nuclei.
- Coagulation and agglomeration of the primary soot particles (20–70 nm) to chain-like structures (100 nm–2 µm).

Due to the complexity of the involved parameters, several factors influence soot formation [13]. One of the main physical factors is temperature, where soot formation often shows a maximum at certain temperatures, as with a further increase in temperature, oxidation of the soot particles becomes more dominant. Pressure also has a significant impact, but this effect is hard to isolate, as with changes in pressure, several combustion parameters, such as flame structure, temperature, and thermal diffusivity, are changed as well. Amongst chemical factors, the oxygen concentration during combustion has a significant influence [13]. The relationship between soot formation and oxygen concentration also shows a maximum value, as oxygen enables the formation of soot precursors through radical reactions but promotes the oxidation of precursors and soot particles at the same time. The composition of the applied fuel also plays a major role; with increasing oxygen and hydrogen content, soot formation decreases [14], while with an increasing fraction of carbon, it increases, and sulfur content seems to have no significant effect on it [13]. Oxygenates in diesel fuels have a strong impact on soot formation. Accordingly, Mueller et al. suggested based on numerical simulations that fuel oxygenation is more effective in soot reduction than increasing the oxygen entertainment from the charge gases [14]. In addition to the already discussed factors, engine design, e.g., the design of the combustion chamber, injection timing and strategy, and intake pressure and temperature, amongst others, also have a dominant effect on particulate formation [13]. Most notably, the application of an exhaust gas recycling (EGR) system, which is implemented to decrease NO_x emissions, increases soot formation in CI engines [10]. Hence, soot is expected to be more of an issue in modern CI engines.

Vyavhare et al. performed investigations with near-edge X-Ray absorption fine structure (XANES) and high-resolution transmission electron microscopy (HR-TEM) of soot particles originating from crankcase oils. XANES analysis demonstrated the presence of zinc polyphosphate in the soot particles, which was interpreted as an indicator of the

removal of the tribofilms, which overcame the rate of film formation by antiwear additives (AW) and resulted in elevated wear [15]. Thersleff et al. investigated soot particles from petrol passenger car and gas turbine engines via scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) [16]. They reported 3–5 nm zinc oxide nanoparticles in the agglomerates containing inhomogeneous pockets of phosphorus and sulfur, which they attributed to the zinc dialkyl dithiophosphate (ZDDP) present in the engine oils.

1.2. The Impact of Soot on Engine Tribology

Studies regarding the influence of soot on selected engine oil parameters are widely reported in the literature. Investigations are often combined with the analysis of AW additives, especially ZDDP, as this additive is commonly utilized in engine oil formulations. ZDDP forms a surface layer, commonly referred to as tribofilm, on the substrate surface, and produces a sacrificial layer which protects the substrate from wear. ZDDP tribofilm formation is a well-researched topic. The few nanometers-thick base layer consists of sulfides, where 50–150 nm thick pads of glassy polyphosphates are deposited on top [17]. Gautam et al. studied the influence of antiwear additive (phosphorus), dispersant, and detergent (sulfonate) levels on the soot formation and wear. Ball-on-disc wear tests were conducted and the wear scars were subsequently analyzed by scanning electron microscopy (SEM) and energy-dispersive X-Ray elemental analysis (EDX) [18]. Wear was found to increase with soot and to decrease with phosphorus content, while dispersant levels had a lower impact, although wear was somewhat reduced at high dispersant levels as well. Furthermore, a predominantly abrasive wear mechanism was suggested [18]. Green and Lewis provided a comprehensive review on the friction and wear in soot-contaminated engine oils [19]. They stated that the predominant wear mechanism of sooted oils is abrasion, but that starvation of the tribocontact and corrosion can also occur in sliding contacts, which further accelerates the material loss. Additionally, it is mentioned that earlier research by Rounds postulated that increased wear can be attributed to the preferential adsorption of ZDDP degradation products on soot agglomerates [20], but later studies revealed that abrasion of the tribofilm is indeed mainly responsible for the increase in wear with soot content, which was also generally observed by several studies, e.g., in a study by Gautam [18].

As real crankcase soot is not readily available, i.e., it requires removal from used oils and subsequent preparation (cleaning), several studies have used carbon black (CB) as a soot surrogate. Hu et al. studied CB as a soot surrogate at various levels in base oils and fully formulated lubricants [21]. They concluded that both the friction and wear properties of the fully formulated oil were better compared to the base oil at all contamination levels and reported a decrease in the coefficient of friction (CoF). Furthermore, they highlighted that the addition of a dispersant to the carbon black-contaminated base oil improved both friction and wear properties [21]. Olomolehin et al. described an antagonistic interaction between ZDDP and CB in model lubricants [22]. They reported higher wear rates for oils containing ZDDP + CB compared to base oil + CB mixtures. They noted that if no preformed film is deposited on the surfaces, the rate of ZDDP film formation becomes the rate-determining step for wear. Kontou et al. investigated the influence of various dispersant types and levels in the presence of CB [23]. They also found that wear increases when ZDDP is present in carbon black- and dispersant-containing base oils. Furthermore, the wear rate increases with phosphorus concentration; hence, it was suggested that ZDDP reacts with the substrate, forming a thin iron sulfide film, which is immediately removed by CB in an abrasive manner. Hence, the zinc polyphosphate cannot form, and this results in an abrasive–corrosive wear mechanism as a whole, controlled by the surface reaction between ZDDP and the substrate. Also, wear had a high dependency on dispersant type and concentration, as first an increase and then a subsequent decrease with dispersants was observed. The increase in wear at low dispersant concentration was attributed to increased mobility of the CB particles, while the decrease at high dispersant concentration

could either be caused by the inhibition of the ZDDP film abrasion by CB, or by reactions in solution between ZDDP and the dispersant, which lowered the reactivity of ZDDP. Salehi et al. also suggested an abrasive–corrosive mechanism for CB- and ZDDP-containing oils [24]. They performed tribological investigations using a base oil (BO) and a fully formulated oil (FFO) containing various CB levels and reported generally increasing wear volume with CB. Surface characterization via EDX and Raman spectroscopy revealed that phosphates in the tribofilm were present without CB in the case of the FFO, but largely absent when CB was added. BO showed a lower wear volume compared to the FFO at the same CB level. Additionally, additive absorption on the CB particles was indicated, but the authors demonstrated that this has less effect on wear compared to the antagonistic interactions between ZDDP and CB. Weimin et al. studied the interaction of soot and ZDDP using model lubricants. Tribometrical investigations and subsequent Raman spectroscopy, EDX, and X-Ray photoelectron spectroscopy (XPS) analyses were conducted. The results revealed increasing wear with soot content, a decreasing concentration of zinc phosphate, and an increasing abundance of sulfur on the substrate surface when soot content was increased. Furthermore, changes in the phosphate structures were observed: sooted oils produced long-chain metaphosphates as opposed to non-sooted oils, where short-chain pyrophosphates were prevalent. The authors attributed this to an increase in contact stress when soot is present, and to the embedment of soot particles on the substrate surface [25].

To summarize, there are currently multiple competing opinions/hypotheses of wear caused by soot particles, as follows:

- Mechanical abrasive wear, which interprets the increased wear through the removal of tribofilm and substrate material simply by a 3-body wear mechanism, [15,18,19] or by starving the tribocontact of oil flow [26].
- Additive binding by soot particles, where the interaction of additives, mostly ZDDP and soot, is suggested, which prevents ZDDP from reaching the tribocontact and forming a film [20,27].
- Tribocorrosion-based wear [22,23], where it is also suggested that the sulfide base layer commonplace in ZDDP films can form on the surface, but it is rapidly removed by the soot particles [24].

Since there is no conclusion in this regard, the presented study aims to further elaborate the wear mechanism caused by soot. Recent studies almost exclusively use CB as a soot surrogate [22–24,27], which is known to be different from crankcase soot [24,28,29]. Furthermore, either experimental formulations [15,22–25] or artificially altered oils [27] are utilized. Although artificially altered oils show a good correlation with used oils from the field when parameters are carefully selected [30,31], differences in oil degradation can also be observed, e.g., regarding elemental composition [31] or wear properties [30].

Studies with both crankcase (engine) soot and oil degradation generated by an ICE are largely absent from the literature, although they would represent the closest simulation of the real tribosystem and, hence, the most reliable data. Accordingly, this study utilizes used oils generated by an engine dynamometer test, which offers several advantages over prior investigations, mainly that a commercially available, state-of-the-art lubricant is used and both the soot formation as well as the oil degradation are performed in a real ICE. This study especially focuses on ZDDP degradation, which is very well understood in fully formulated lubricants [32]. Degradation of ZDDP-containing engine oils during real driving conditions is generally well documented, and studies regarding the chemical properties and additive degradation [33] and the resulting tribological properties and tribofilm formation [34] are available. In these cases, high-resolution mass spectrometry (HR-MS) is used to accurately describe the additive degradation on a molecular level, and XPS is used to characterize the surface films, which together allow for a comprehensive assessment of most tribologically relevant parameters. Additive binding on soot particles and uncovering potential correlations between film formation, wear, and soot, as well as interferences between soot and common conventional analytical methods, are also

highlighted. Additionally, the comparison of analytical data with and without soot offers an indication for operators on how to generate more accurate oil condition monitoring results.

2. Materials and Methods

2.1. Engine Dynamometer Test

The engine dynamometer test was conducted based on ASTM D7484 Stage A [35] to derive the sooted oil samples. A deviation from the standard was the fixed duration of the dynamometer test, namely 100 h. This, in conjunction with the sampling of the engine oil every 10 h, was selected to generate a sample set with varying soot content. This sample matrix enables the in-depth study of the effects of soot, as several different concentrations are available; hence, comparable soot loadings to various drivetrains can be selected from it. The engine dynamometer test was started with approx. 17 L (4.5 US liquid gallons) of fresh oil. Nine intermediary samples were taken, each consisting of 250 mL (2.25 L in total). No fresh oil was added during the dynamometer test. This way, around 13% of the total oil volume was removed by intermediary sampling, which is below the usual difference between minimum and maximum oil levels in common engines.

Engine operation was conducted with a diesel fuel according to the specifications described in ASTM D975 [36]. During the test, the Cummins ISB medium-duty diesel engine was kept at constant operating parameters for the 100 h, where the injection timing was retarded to approx. -15° to promote soot formation. Table 1 gives an overview of the properties of the engine, and Table 2 displays the operating parameters during the dynamometer test.

Table 1. Properties of the utilized test engine.

Test Engine	
Manufacturer	Cummins
Model	ISB
Configuration	Inline 6
Displacement (L)	5.9
Aspiration	Turbocharged
Fuel system	High-pressure common rail direct injection
Fuel	According to ASTM D975 [36]
Injection timing	Retarded to -15°
Exhaust system	Cooled exhaust gas recirculation (EGR)

Table 2. Parameters of the engine operation during the dynamometer test.

Engine Operating Parameters	Engine Speed (RPM)	Torque (NM)	Fuel Rate (kg/h)	Fuel Temp. ($^\circ\text{C}$)	Coolant Outlet Temp. ($^\circ\text{C}$)	Coolant Pressure (kPa)	Intake Manifold Pressure (kPa)
Average	1600	419	20	40	99	104	217
Min.	1597	406	19	33	98	103	206
Max.	1603	443	21	40	100	106	226
Engine Operating Parameters	Intake Manifold Temp. ($^\circ\text{C}$)	Inlet Air Temp. ($^\circ\text{C}$)	Turbo Outlet Temp. ($^\circ\text{C}$)	Oil Temp. (pan) ($^\circ\text{C}$)	Oil Pressure (kPa)	Intake Restriction (kPa)	Exhaust Back Pressure (kPa)
Average	68	30	152	110	183	2.0	7.4
Min.	66	25	122	109	151	0.6	5.4
Max.	70	34	160	116	204	2.2	7.9

2.2. Engine Oil and Oil Condition Monitoring

A commercially available 0W-20 engine oil suitable for both modern petrol and diesel engines was used. The engine oil corresponds to the specifications of VW 508.00/509.00

and contains both phenolic as well as aminic antioxidants (AOs), ZDDP AW, and calcium carbonate base reserve in a fully synthetic base oil. A 200 mL oil sample was collected every 10 hours for chemical analysis until 90 h, and eventually the whole oil sump was drained at 100 h, resulting in 10 “sooted oil” samples in total, together with the fresh oil. Table 3 shows the key physiochemical parameters of the engine oil.

Table 3. Properties of the utilized engine oil.

Engine Oil	
NN (mgKOH/g)	1.9
TBN (mgKOH/g)	6.4
Dynamic viscosity at 40 °C (mPa × s)	35.8
Dynamic viscosity at 100 °C (mPa × s)	6.1
Density at 40 °C (g/mL)	0.824
Density at 100 °C (g/mL)	0.786
Viscosity index (—)	147.1
Ca content (ppm)	1900
P content (ppm)	700
S content (ppm)	1900
Zn content (ppm)	800

The authors previously developed a comprehensive methodology to characterize engine oil degradation, where the various applied methods are described in detail in [33,34]. Accordingly, only a brief summary of the chemical and tribological characterization is given below.

2.2.1. Soot Removal and Extraction

Soot from selected samples was removed via centrifugation to enable a direct comparison of the chemical and tribological properties of samples with and without soot. Then, 50 g of the used oil samples were centrifuged at 13,000 rpm for 96 h and tempered at 40 °C without the addition of any solvent, using a Fiberlite F15-6x100y rotor (ThermoFisher, Waltham, MA, USA). The applied parameters correspond to 18516 g relative centrifugal force. Subsequently, 10 g aliquots of centrifuged oil were carefully removed from the top of the vials. The top 10 g aliquot was also characterized according to the methodology described in Section 2.2.2–Section 2.4 (“centrifuged oils”). The fresh oil underwent the same centrifugation process to determine the effects of centrifugation on the oil additives. Subsequently, the bottom 10 g aliquot (containing most of the soot) was washed with solvent to determine the n-heptane insoluble fraction of the sooted engine oils according to the method presented in [33]. In total, 3 washing steps were completed, each with 30 g n-heptane, where the mixtures were first homogenized by vigorous shaking, then centrifuged for 4 h while being tempered at 40 °C. The n-heptane insoluble contents were determined gravimetrically after drying the vials in an oven at 80 °C.

Adsorption of additives and other chemical species on the soot particles was also investigated. In doing so, the isolated and dried soot samples were extracted via toluene and 2-propanol in an ultrasonic bath at 40 °C for 30 min. Subsequently, the solutions were filtered through a 0.1 µm cellulose nitrate membrane filter to remove the soot particles. The liquid extracts were then analyzed according to the procedure described in Section 2.2.3. Additionally, the elemental composition of the extracted and dried soot samples was investigated using SEM-EDX by utilizing a JSM-IT500 scanning electron microscope (JEOL, Peabody, MA, USA). The instrument was operated under UHV conditions, with 10.0 kV acceleration voltage. Data from EDX analyses were collected from an approx. 300 × 300 µm² area in all cases.

2.2.2. Conventional Oil Analysis—Methodology

The investigation of conventional oil parameters focused on easy-to-obtain established parameters, which describe overall trends regarding oil degradation. This consisted of

Fourier transformed infrared spectroscopy (FTIR), acid–base titrations, inductively coupled plasma–optical emission spectroscopy (ICP-OES), and determination of viscosity and density. Table 4 provides a detailed overview of the measured characteristics, applied methods, and the corresponding standards and equipment.

Table 4. Applied conventional oil analysis methods.

Parameter	Analytical Technique	Equipment
Oxidation	FTIR at 1720 cm ^{−1} (in-house method [33,34])	Tensor 27 FTIR spectrometer (Bruker, Ettlingen, Germany)
Nitration	FTIR at 1630 cm ^{−1} (DIN 51453 [37])	
Soot loading	FTIR at 2000 cm ^{−1} (ASTM E2412 [38])	
Residual phenolic antioxidants	FTIR at 3650 cm ^{−1} (in-house method [12,33])	
Residual aminic antioxidants	FTIR at 1515 cm ^{−1} (in-house method [12,33])	
Residual ZDDP	FTIR at 1020–920 cm ^{−1} (in-house method [12,33])	KF coulometer 756 and an oven sample processor 774 (Metrohm AG, Herisau, Switzerland)
Water content	Indirect Karl-Fischer titration (DIN 51777 [39])	
Total base number (TBN)	Potentiometric indication titration (ISO 3771 [40])	
Neutralization number (NN)	Color-indication titration (DIN 51558 [41])	-
Elemental composition	ICP-OES (in-house method [12,33])	iCAP 7400 ICP-OES duo (ThermoFisher, Waltham, MA, USA)
Kinematic viscosity and density at 40 °C and 100 °C	Stabinger viscometer (ASTM D7042 [42])	Stabinger SVM 3000 viscometer (Anton Paar GmbH, Graz, Austria)
Viscosity index (−)	Stabinger viscometer (ASTM D2270 [43])	

FT-IR spectra were averaged from 32 transmission measurements, water content, TBN and NN from 2 independent determinations, and ICP-OES results from 3 repetitions on 3 independent wavelengths. For all conventional measurements, the validation criterion was that the standard deviation did not exceed 10% of the mean value.

Additionally, the rheological properties of selected samples were measured to determine the dependency of the viscosity on the shear rate, i.e., non-Newtonian behavior, of the oil samples. This was conducted via an MCR 302 Rheometer (Anton Paar GmbH, Graz, Austria). The instrument was operated at 40 °C, with a 25 mm plate-on-plate configuration. A flow curve from 1 to 1000 s^{−1} shear rates was measured.

2.2.3. Advanced Oil Analysis—Methodology

Additive degradation and adsorption on the soot particles was further characterized via HR-MS. Similar to conventional oil analysis, the full description of the applied method is available in [32,33].

As solvent, a methanol–chloroform mixture (volumetric ratio 3:7) was used, where the samples were dissolved using a dilution factor of 1:1000. Then, direct infusion at a flow rate of 5 µL/min was used to inject the sample solutions into a LTQ orbitrap XL hybrid tandem high-resolution mass spectrometer (ThermoFisher, Waltham, MA, USA)

Electrospray ionization (ESI) was applied as the ionization method, both in negative and positive ion modes. Low-energy collision-induced dissociation (CID) was performed using a helium collision gas (also used as a cooling gas). As a detector, orbitrap was used to detect parent ions as well as fragments at a resolution of 60,000 at full width and at half maximum. The mass-to-charge (m/z) ratios were measured with an accuracy of 5 ppm or greater.

Data analysis and interpretation were performed with Xcalibur (2.0.7) and Mass Frontier (6.0) (ThermoFisher, Waltham, MA, USA).

2.3. Tribometrical Characterization—Methodology

The methodology is discussed to a greater detail in [34]. Table 5 shows the relevant measurement parameters. An SRV[®] 4 model tribometer (Optimol Instruments Prüftechnik, Munich, Germany) was used to determine the CoF and wear properties of selected used and centrifuged oil samples. To determine wear properties more accurately, the surface of all test specimen was polished ($R_a \sim 0.1 \mu\text{m}$) before the experiments. Subsequently, the test specimen was cleaned in a 0.05 M disodium ethylenediaminetetraacetate (EDTA) solution to remove the tribofilm (adsorbed organic species). Three-dimensional topography data were collected at approx. 2 nm vertical and 150 nm lateral resolution by a Leica DCM8 microscope (Leica Microsystems, Wetzlar, Germany) as described in detail in [44]. All reported data are based on 3 experiments per oil sample if not indicated otherwise.

Table 5. Configuration and operating conditions of the tribometrical experiments.

Tribometrical Experimental Parameters			
Oil quantity (mL)	~0.1	Temperature (°C)	100
Contact	Ball-on-disc	Mode	Oscillation
Material (ball and disc)	100Cr6	Hardness (ball and disc)	HRc 62
Ball dimension (mm)	10	Disc dimensions (mm)	10 × 7.9
Load (N)	50	Stroke (mm)	1
Mean contact pressure (GPa)	1.2	Maximum contact pressure (GPa)	1.7
Frequency (Hz)	30	Duration (min)	120

2.4. Tribofilm Composition via XPS

XPS was used (via a theta probe angle-resolved X-Ray photoelectron spectrometer, ThermoFisher, Waltham, MA, USA) to identify and quantify various elements adsorbed on the SRV[®] discs, i.e., the composition of the tribofilm after the SRV[®] experiments according to the method described in detail in [34]. Single-spot (size 100 μm) measurements at the middle of the wear scar as well as depth profiling and surface mapping of selected samples were performed. In all cases, UHV conditions and a monochromatic Al K α radiation source ($h\nu = 1486.6 \text{ eV}$) were utilized at 50 eV pass energy, with a 0.1 eV step size. In the cases of the single-spot and surface map measurements, first, <1 nm of the sample surface was removed by 10 s sputtering with Ar⁺ (3 kV, 1 μA) ion bombardment. Depth profiling was performed with sputtering steps until approx. 70 nm depth from the initial surface had been reached. XPS measurements were performed before the 3D topography data collection, i.e., prior to the EDTA cleaning of the SRV[®] test specimens.

3. Results and Discussion

3.1. Conventional Oil Analysis—Results

Figure 1a shows the soot loading in the final sooted oil (highest soot loading) over the centrifugation time (double determination). The values indicate that 1 day of centrifugation was not able to completely remove the soot from the oil samples; however, 2 days seem to be effective in this regard. Additionally, no major changes are observable between 2 days and 4 days. Still, for the purpose of this study, a centrifugation time of 4 days (96 h) was used uniformly for all oil samples to ensure soot removal. Figure 1b compares key oil parameters of the fresh oil before and after centrifugation. This analysis was performed to investigate the effects of centrifugation on oil additives (additive separation). All relative values are close to 100%—in fact, NN, TBN, viscosity, density, and Zn content barely changed during the centrifugation. There is a minor reduction visible in Ca, and also a minor increase in P and Zn; however, this can also be attributed to the reproducibility of the applied ICP-OES method. Overall, the results indicate that both the physical and chemical properties of the fresh oil remain largely unaffected by the centrifugation process.

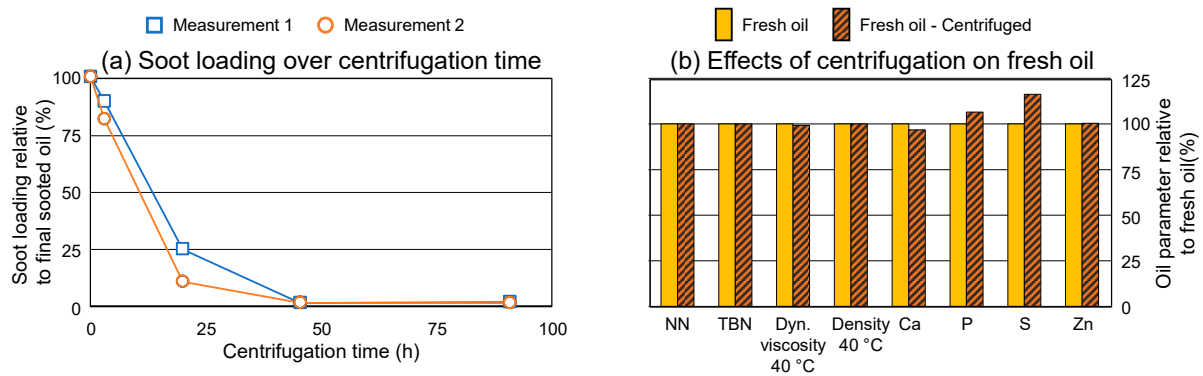


Figure 1. (a) Soot loading over centrifugation time in the final sooted oil (highest soot loading); (b) effects of centrifugation on key oil parameters on the fresh oil.

This chapter provides an overview of commonly determined oil degradation parameters. The high soot loading present in some sooted oil samples caused difficulties for some measurements; accordingly, sooted and centrifuged oils are presented side-by-side to give an accurate picture of the parameters, as well as the potential problems when using conventional measurements.

Figure 2a displays the FTIR absorption spectra of selected sooted and centrifuged samples after 10, 50, and 100 h runtimes on the engine dynamometer. The intensive baseline shift is indicative of the soot loading of the samples—determination according to ASTM E2412 is based on the height of the baseline at 2000 cm^{-1} [38] (indicated by the dotted line). Furthermore, due to the high absorption of the samples with higher soot loading, total absorption can be observed in some cases (e.g., the 100 h sooted oil), which results in very high noise in some spectral regions, e.g., $4000\text{--}3000\text{ cm}^{-1}$. Comparatively, centrifuged oils display practically no baseline shift and are generally comparable to the fresh oil. This shows that the applied centrifugation successfully removed most of the soot particles from the sooted oil samples. In numerical terms, the sooted oils displayed a soot loading of $22.5\text{--}232.0\text{ A/cm}$, while the centrifuged samples show a marginal loading of $1.5\text{--}3.2\text{ A/cm}$. Figure 2b shows both the soot loading determined by FTIR as well as the gravimetrically determined n-heptane insoluble content of the sooted oil samples. Both parameters increase in a close-to-linear manner during the engine dynamometer test, which is expected, as soot is a byproduct of fuel combustion [33], usually originating from inhomogeneous, fuel-rich regions around the injected fuel jet [13,14]. Since the engine parameters, including fuel flow, were close to constant during the 100 h period, it is expected that soot accumulates in a linear manner (see Table 2). It is noteworthy that the soot determination via FTIR and via centrifugation and subsequent gravimetrical analysis show a very comparable, almost identical, propagation. The final sample displayed a soot loading of 232.0 A/cm which corresponds to approx. 7.8 m% of soot. This aligns with the data reported by Lockwood et al., who found up to 7.5 m% soot in heavy-duty diesel engines at extended oil mileages [45] and with Green et al., who expected a soot content of up to 10% by 2010 [19]. However, this is significantly higher than diesel passenger cars, where field studies found up to approx. 45 A/cm of soot loading [12]. Comparatively, petrol-fueled passenger cars generally display significantly less soot, e.g., previous field studies found only 1.5 m% in a turbocharged petrol-fueled passenger car at the end of the oil change interval [33] and below 5 A/cm in a petrol-fueled passenger car fleet [12].

Figure 3a,b compares the determined oxidation and nitration in the sooted and centrifuged oils, respectively. As shown, oxidation displayed a severe interference at higher soot loading in the sooted oil samples, where nonsensical (negative) values were also found. This is due to the already mentioned total absorption in the FTIR spectra between 4000 cm^{-1} and 3000 cm^{-1} (see Figure 2a, as several integration methods are using this range to determine the baseline). The centrifuged oil samples show no such interferences as soot was removed; accordingly, evaluation of the oxidation was possible. The oil samples

display a close-to-linear increase in the oxidation with the runtime in the engine dynamometer test, where a low final value of approx. 3 A/cm is reached. Comparatively, a previous field study reported up to 8 A/cm oxidation in diesel-fueled passenger cars at the end of the oil change interval [12]. Comparatively, the measured 3 A/cm in the final sample would indicate approx. 5000 km mileage in a diesel passenger car, which is far below common OEM oil change intervals. Oxidation is usually higher in petrol engines than in diesel engines, which can be attributed to the lower air–fuel ratio (less excess air) and the higher abundance of active combustion byproducts (radicals) [12]. Comparing the final sooted oil sample to data on petrol vehicles reported in [33] and [12], the measured 3 A/cm would indicate only 1000–2000 km mileage.

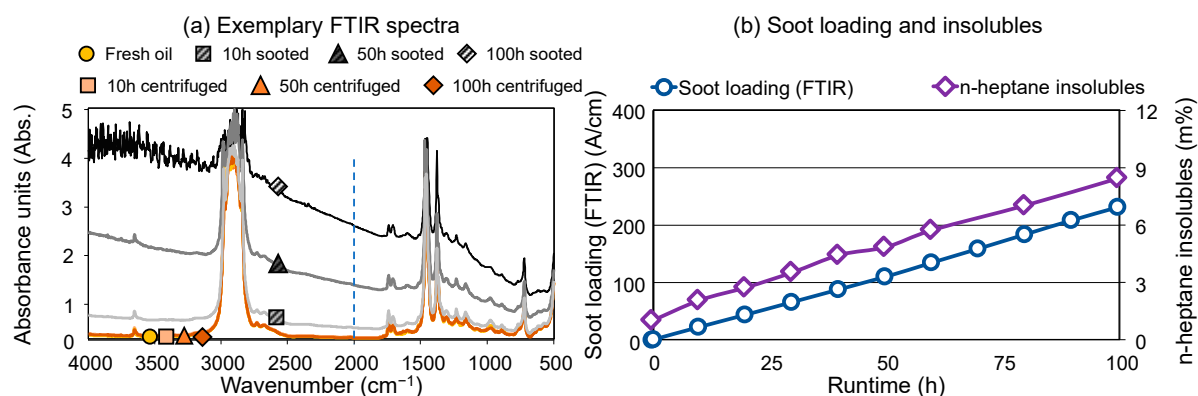


Figure 2. (a) Exemplary FTIR spectra of selected sooted and centrifuged oils; (b) soot loading (FTIR) and n-heptane insolubles.

Nitration does not seem to display spectral interferences with soot, as the propagation and values of the sooted and centrifuged oils are comparable, at 2.2 A/cm and 3.3 A/cm for the 100 h samples, respectively. Nitration also remains relatively low during the engine dynamometer test, which is expected, as diesel engines usually display only minor nitration in the engine oil [12]. The nitration of the final sooted oil is somewhat higher than previous field studies on diesel vehicles, e.g., [12] reports approx. 2 A/cm nitration between 10,000 and 15,000 km. Nevertheless, the final nitration value is below that found in the typically used petrol engine oils, where approx. 25 A/cm is reported at 20,000 km in [33].

Figure 3c,d illustrates the residual contents of ZDDP AW, phenolic AO, and aminic AO, relative to the fresh oil (corresponding to 100%). These additives were selected, since they are very commonly utilized in fully-formulated oils and cover two very important additive functions, namely protection against oxidation and wear, both greatly effecting the useful life of the lubricant. Additionally, it has to be mentioned that no further AOs or AWs were identified in the fresh oil via FT-IR or HR-MS (see Section 3.2). The combination of phenolic AOs (usually sterically hindered butyl-hydroxy-toluene derivatives) and aminic AOs (usually diphenylamines) is common, as there are synergetic effects between the structures. Peroxy radicals are displaying a higher reactivity with aminic AOs, but the formed amine radicals are relatively instable [46]. Subsequently, the used up aminic AO is regenerated by the phenolic AO, which forms a stable phenoxy radical [33].

Once again, interferences are visible in case of higher soot loading for the evaluation of the phenolic AOs, as the final three samples (80–100 h) display either values over 100% or negative antioxidant content. This is once again caused by the aforementioned total absorption caused by soot in the spectral range of 4000 cm⁻¹ to 3000 cm⁻¹, as the phenolic AOs are evaluated at 3650 cm⁻¹ (see Figure 2 and Table 4). However, once soot is removed by centrifugation, evaluation becomes possible. The centrifuged oils show that approx. 80% of both phenolic and aminic AOs and approx. 60% of the ZDDP AW are still present in the engine oil after 100 h utilization in the engine. The values for aminic AOs and ZDDP

AW are comparable between sooted and centrifuged oil, as no interferences with soot were present when evaluating these species.

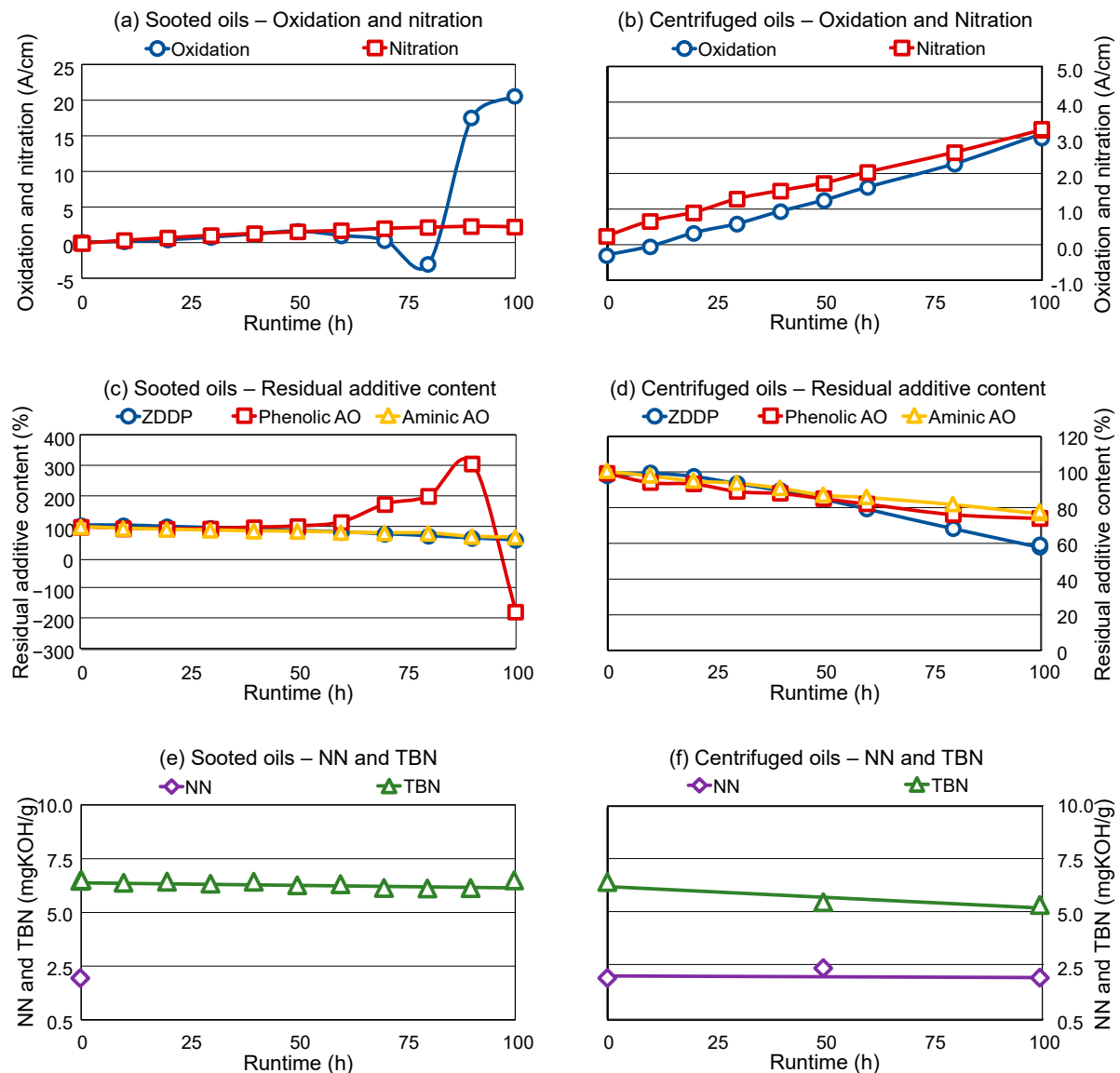


Figure 3. (a,b) Oxidation and nitration of the sooted and centrifuged oils; (c,d) residual additive content in the sooted and centrifuged oils relative to the fresh oil; (e,f) NN and TBN of the sooted and centrifuged oils.

Figure 3e,f gives an overview of the NN and TBN during the engine dynamometer experiment. TBN is constant and comparable to the fresh oil in the sooted oils, while the determination of NN was impossible with the applied color indication titration due to the extremely dark used oil samples. As the applied TBN method uses a potentiometric indication, no such problems were present during the base reserve measurements in the sooted oils. The centrifuged samples show a minor TBN decrease (from 6.4 to 5.5 mg KOH/g), which is most likely caused by the centrifugation. The base reserve (calcium carbonate) is not dissolved in the engine oil, but dispersed by the detergents, and, accordingly, can be removed to some degree. The NN determination was successful for the centrifuged samples, and the NN is comparable to the fresh oil after 50 h and 100 h as well.

Overall, the results show that the oil did not suffer a high degree of oxidative degradation in the engine, as oxidation remains low, NN and TBN are comparable to the fresh

oil, and the AO and AW additives are present to a high degree at the end of the engine dynamometer test. However, determination of several parameters was not possible at higher soot loadings, and was only possible only once soot was removed via centrifugation.

The dynamic viscosities of the sooted and centrifuged oils are depicted in Figure 4a,b, respectively. The sooted samples display an increase in the dynamic viscosity with increasing runtime (increasing soot loading), which results in an over 50% increase compared to the fresh oil at 40 °C. The viscosity at 100 °C shows identical trends. Lockwood et al. and George et al. also reported a significant increase in viscosity with the soot content of CI engine oils [45,47]. An increase in viscosity can be caused by the oxidation and subsequent partial polymerization of the oil matrix [33], but this seems improbable in this case, as the oxidation of the oils is minor (see Figure 3b). Accordingly, this increase in viscosity can be directly attributed to the soot present in the samples, especially as the centrifuged oils show a minor decrease of approx. 15% (such a decrease is commonly attributed to the partial degradation of the viscosity modifier and viscosity index improver additives [12]).

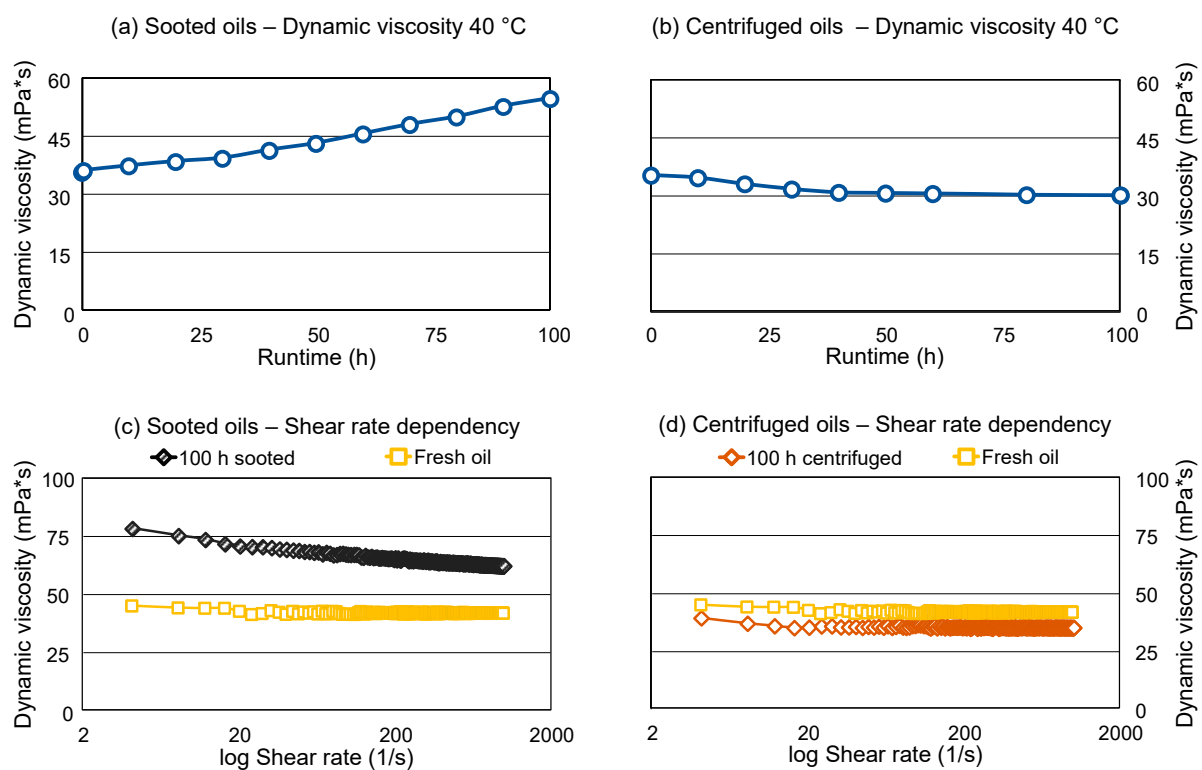


Figure 4. (a,b) Dynamic viscosity of the sooted and centrifuged samples; (c,d) shear-rate dependency of the viscosity of the final sooted and centrifuged sample.

Figure 4c,d displays the flow curves of the fresh, final sooted, and final centrifuged oil samples. A flow curve is measured by a rheometer, at different controlled shear rates, which is not the case during viscosity measurements, as the shear rate is usually not controlled in a viscometer. Viscosity dependency on the shear rate is commonly referred to as “non-Newtonian behavior”. As shown, the viscosity of the fresh engine oil has only negligible dependency on the applied shear rate, meanwhile, the final sooted oil shows a higher viscosity which decreases with increasing shear rates, and which, accordingly, behaves in a non-Newtonian manner. This could be caused by structural viscosity effects, e.g., the breakdown of soot particle agglomerates in the sooted oil sample. Kontou et al. found similar shear-rate dependency, which they also attributed to the breakdown of loose aggregate structures [23]. Comparatively, the viscosity of the final centrifuged oil sample shows only minimal dependency on the shear rate and is overall similar to the fresh oil, although marginally lower. Hence, the thickening and non-Newtonian behavior of the

sooted oil sample also directly results from the soot loading. This also highlights potential problems during routine engine oil condition assessment. Conventional viscosity measurement techniques might give unreliable results if a high amount of soot is present, as the shear rate is usually not controlled in viscometers, which are designed for the measurement of Newtonian fluids. However, the general trends of the viscosity measurements in the applied viscometer and rheometer are similar. The sooted oils display a significant increase in viscosity, which is reversible once the soot is removed.

Figure 5a shows the elemental composition of the sooted oils. The applied ICP-OES measurement is not affected by soot loading, as the samples are prepared via microwave-assisted digestion with nitric acid and hydrogen peroxide, which completely oxidizes the soot particles into CO₂. Common additive elements, such as calcium (base reserve), phosphorus, sulfur, and zinc (all ZDDP) display a close-to-constant concentration during the engine dynamometer test. Comparatively, iron, which is indicative of engine wear, shows a steady increase through the utilization of the engine oil [45]. It shows that wear indeed takes place in the engine as the soot loading increases, despite the otherwise minor oil degradation (e.g., low oxidation and NN, high TBN and residual AW content). Compared to previous field studies [12], the 40 ppm iron content would be indicative of approx. 10,000 km of on-road utilization in diesel passenger cars, and petrol vehicles only reached around 20 ppm under close to 20,000 km of on-road utilization. Accordingly, in on-road vehicles, 40 ppm iron can be considered rather high, especially since further iron is expected to accumulate in the oil filter in the form of particles. This highlights the somewhat puzzling condition of the sooted oils: despite the low abundance of degradation products and high residual additive levels, the engine wear (iron content) is strongly elevated.

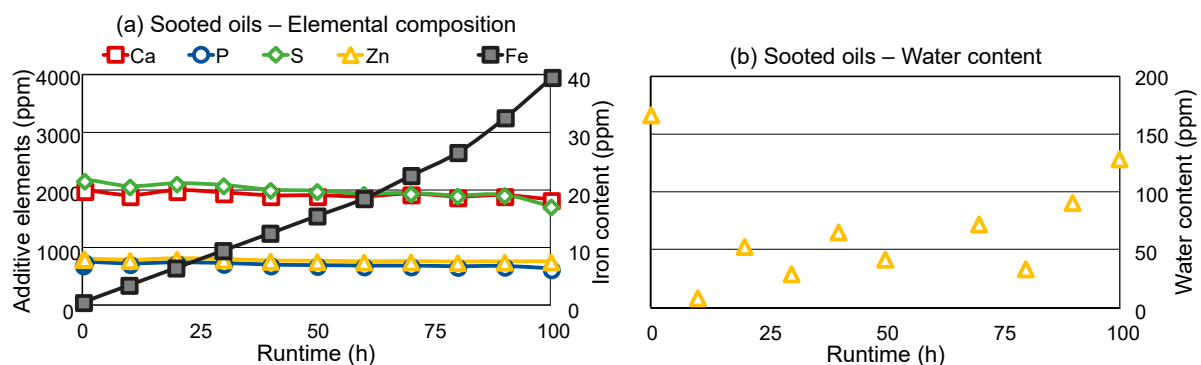


Figure 5. (a) Elemental composition of the sooted oils; (b) water content of the sooted oils.

The water content of the sooted oil samples is displayed in Figure 5b. The applied indirect Karl-Fisher titration is also not influenced by soot, as the water from the oil samples is evaporated in an oven and carried over to the titration cell by a nitrogen carrier gas stream; accordingly, soot particles do not reach the titration solution. The water content of the samples is low, in the range of 10–170 ppm, which is well below previously reported values for fleet studies with diesel engines, where up to approx. 1200 ppm water was found in used oils in long-range operation [12]. Accordingly, no clear trend can be derived in this regard. Here, petrol engines in long-range operation had up to approx. 600 ppm water, and in short-range conditions (frequent cold starts), they had over 2000 ppm. The overall lower water content in the engine dynamometer test can be explained by the close-to-constant operating conditions. On the dynamometer, the average oil pan temperature was measured to be 110 °C (see Table 2), and the lowest recorded temperature was 106 °C. As the oil sump temperature was constantly above the boiling point of water, no strong water accumulation could take place. Water is expected to evaporate under these conditions with the exhaust gas stream [12].

3.2. Advanced Oil Analysis—Results

For the analysis of the lubricant samples via HR-MS, ESI as the ionization method and direct infusion were selected. The main reason for this approach is the accuracy of HR-MS, which is capable of structure analysis without time-consuming separation methods (e.g., HPLC), even in very complex samples. However, the HR-MS results only indicate relative quantities.

Mass spectrometry methods can often be affected by ion suppression. This effect is well-researched, e.g., the review of Furey et. al. [48] gives a comprehensive overview. ESI is affected by ion suppression to a higher degree compared to atmospheric pressure chemical ionization (APCI). Ionization in ESI happens on the droplet surface, and ions are transferred to the gas phase, while with APCI the ionization takes place in the gas phase [48]. Accordingly, the surface activity of species can greatly influence the ionization efficiency when ESI is applied [48]. In general, the following effects can lead to ion suppression in ESI [48]:

- An increase in viscosity and surface tension due to high concentrations, which hinders transfer in the gas phase.
- Competition between analytes and/or matrix components for the available charge.
- The co-precipitation of analytes with non-volatile compounds.

Ionic species (salts) are commonly characterized as ion suppressants [48,49] since they have a high surface activity. Figure 6 gives an overview of the identified additives in the fresh engine oil and the final sooted and final centrifuged oil samples. Multiple aminic AOs, namely alkylated diphenylamines (Figure 6a, positive ion mode) were detected, e.g., m/z 296.237 and 422.378. The structures show a slight depletion after the engine dynamometer test but are still detectable at a higher abundance. Similarly, they are still present in the final centrifuged sample. This corresponds well with the findings of the FTIR analysis, where residual levels of approx. 80% compared to the fresh oil were found (see Figure 3d). The detailed analysis of the phenolic antioxidants was not possible with the applied HR-MS method, as ZDDP species inhibited the ionization of the phenolic antioxidants. This can be attributed to the chemical structure of ZDDP: salts often act as ion suppressants [48,49]. ZDDP has a higher surface activity compared to other common oil additives. The dialkyl dithiophosphate ion has a “polar head–apolar tail” structure; hence, it is expected to accumulate on the droplet surface in the ESI to a greater extent compared to other compounds, and will also display a higher ionization efficiency if present. Sulfonate detergents were also present in the engine oil samples (Figure 6b, negative ion mode). The additives have different alkyl sidechains, e.g., $C_{20}H_{43}$ (m/z 437.310), $C_{22}H_{45}$ (m/z 465.341), and $C_{24}H_{49}$ (m/z 493.373). Similarly, ionization effects between ZDDP and sulfonate detergents were also present. This results in a seemingly higher abundance in the final sooted and centrifuged oils, since ZDDP was partially degraded at this point and inhibited the ionization of sulfonates only to a lesser extent. Nevertheless, the sulfonate detergents were reliably detected in all three oil samples. Figure 6c (negative ion mode) gives an example of the salicylate detergents present. Here, a salicylate with $C_{18}H_{37}$ alkyl sidechain is visible (m/z 389.306), but other alkyl sidechains, e.g., $C_{14}H_{29}$ were also detected (m/z 333.243). The aforementioned ionization effects due to ZDDP also impacted the measured intensity of the salicylate detergents to a lesser extent than the sulfonate detergents; still, the salicylate detergents do not show a great extent of degradation over the engine dynamometer test, as they are present in all three oil samples with a higher abundance.

ZDDP additives are shown in Figure 6d (negative ion mode). The main components of the antiwear solution are propyl-hexyl dithiophosphate (m/z 255.065), dipropyl dithiophosphate (m/z 213.018), and dihexyl dithiophosphate (m/z 297.112). Furthermore, traces of dioctyl dithiophosphate (m/z 353.174) were also found (intensity zoomed in 10 times in the relevant region). The detected dithiophosphates display some depletion but are still present in the final sooted and centrifuged oil samples, once again corroborating the

findings of the FTIR spectroscopy, where residual levels of approx. 60% were found (see Figure 3d).

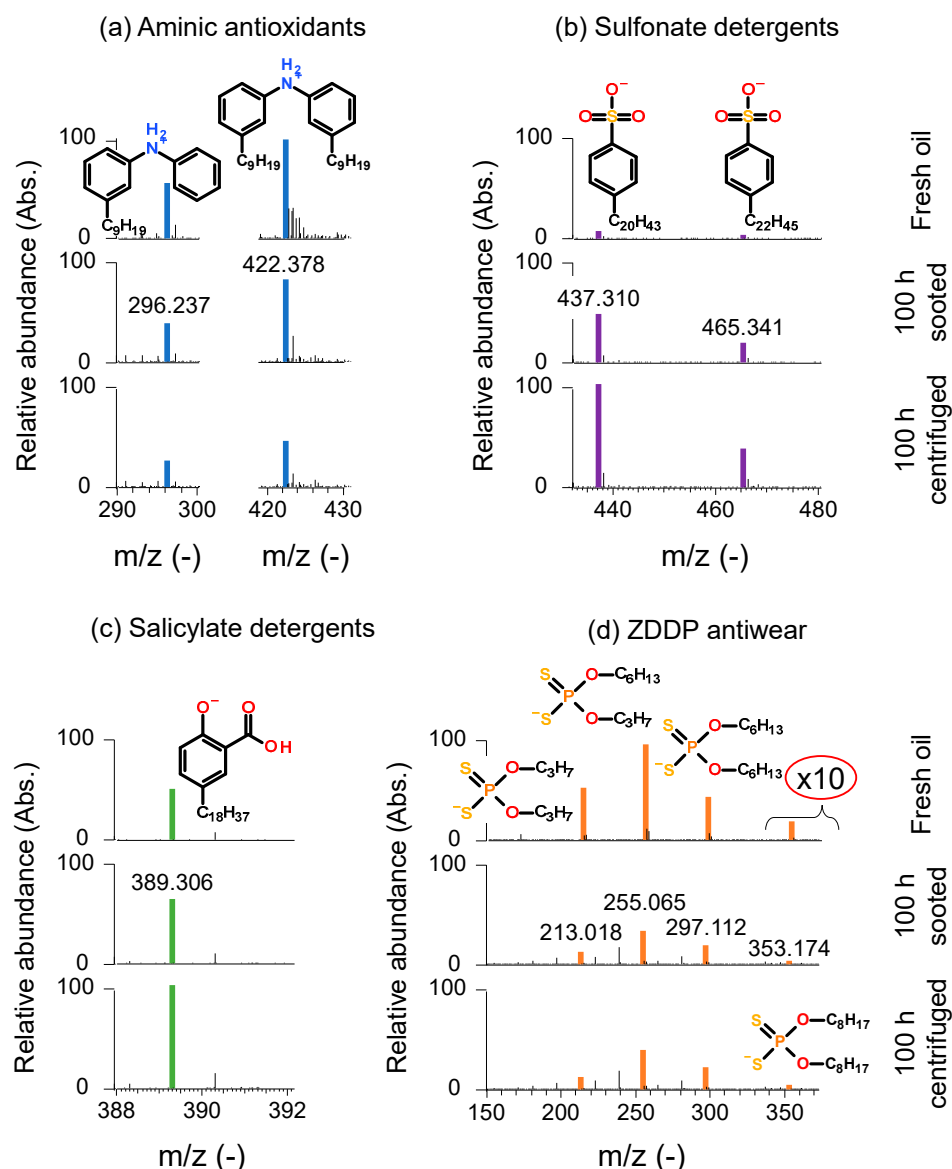


Figure 6. Additive structures in the fresh, final sooted, and final centrifuged oil samples. (a) Aminic antioxidants (positive ion mode); (b) sulfonate detergents (negative ion mode); (c) salicylate detergents (negative ion mode); (d) ZDDP antiwear (negative ion mode).

Overall, the final sooted and centrifuged oils seem to show only mild additive degradation. All identified additives are detectable in both of the used samples; accordingly, the oil degradation seems to be in a relative early state. This corresponds to the findings of the conventional oil analysis, where only minor oxidation and nitration, high residual additive levels, and no significant changes in NN and TBN were detected.

Figure 7a (negative ion mode) shows the main ZDDP component, propyl-hexyl dithiophosphate ("1"; m/z 255.065), and its respective degradation products. The degradation of ZDDP in an ICE is well understood and documented [32,33]. First, dialkyl dithiophosphates oxidize, which results in the origination of dialkyl phosphates, where a sulfur atom is substituted by oxygen in the structure. Subsequently, a further substitution occurs, resulting in dialkyl phosphates. Further oxidation yields alkyl phosphates and finally sulfuric and phosphoric acid. The picture presented in Figure 7a is indicative of an early stage of ZDDP oxidation. Although propyl-hexyl thiophosphate ("2"; m/z 239.088) and propyl-hexyl

phosphate (“3”; m/z 223.110) are detectable at the end of the engine dynamometer test and in the centrifuged sample, the original additive structure is also present. Comparatively, previous studies from Dörr et al. reported the complete depletion of the original dialkyl dithiophosphates after 6000 km in a field study [33] and after 4 h of artificial alteration [32]. Agocs et al. published similar field study results, where the original ZDDP additive completely depleted under 1000 km of mileage in petrol vehicles in city traffic and was only present in trace amounts in diesel vehicles after approx. 5000 km of highway traffic.

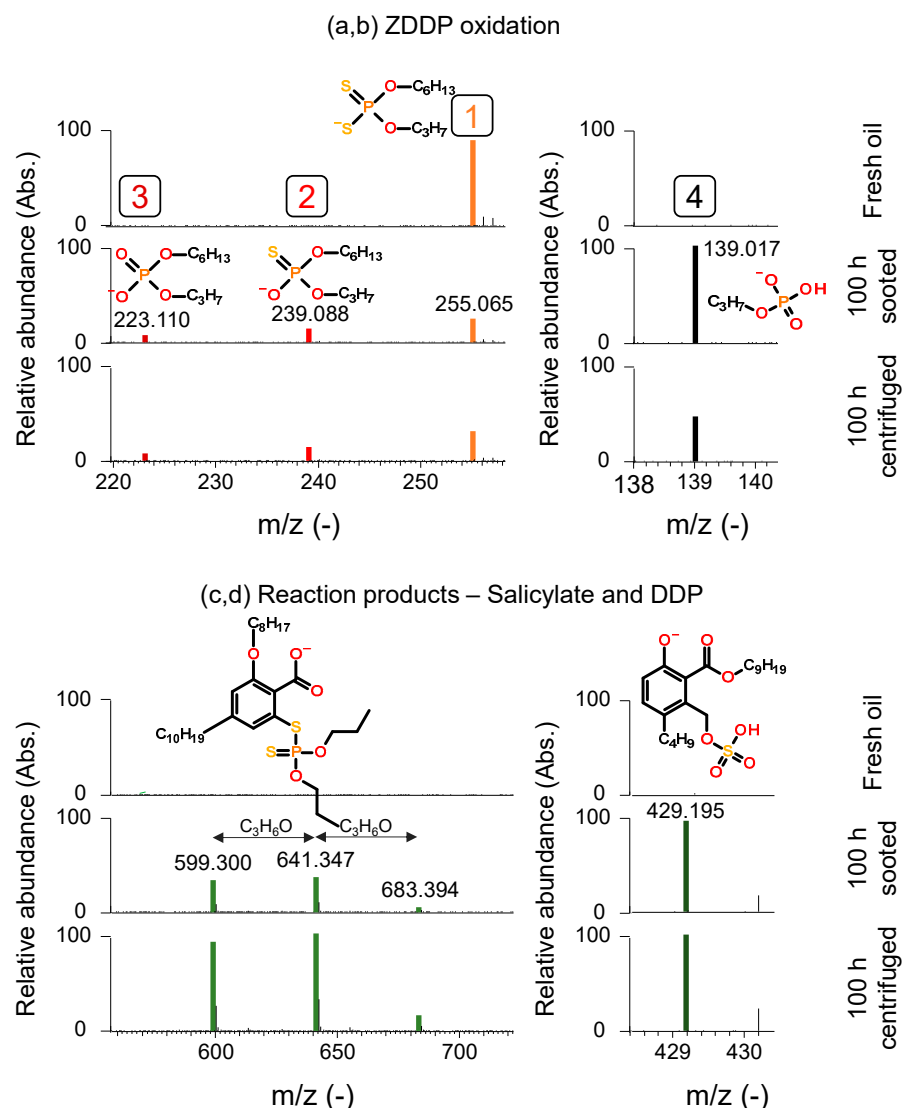


Figure 7. ZDDP Degradation products in the fresh, final sooted and final centrifuged oil samples. (a) Dialkyl thiophosphates and dialkyl phosphates (negative ion mode); (b) alkyl phosphates (negative ion mode); (c) reaction products of salicylate detergents and dialkyl dithiophosphates (negative ion mode); (d) reaction products of salicylate detergents and sulfuric acid (negative ion mode).

Figure 7b (negative ion mode) gives an indication of a further oxidized degradation product, propyl phosphate (“4”; m/z 139.017), which is also present in the final sooted and centrifuged samples, indicating further ZDDP degradation. Generally, all identified dialkyl dithiophosphate species (Figure 6d shows a comparable degradation pattern), namely dipropyl dithiophosphate (m/z 213.018), dihexyl dithiophosphate (m/z 297.112), and dioctyl dithiophosphate (m/z 353.174), remained detectable in the final sooted and the final centrifuged oils, while the origination of the respective dialkyl thiophosphates and dialkyl phosphates was also detected. Additionally, reaction products between the salicylate detergents and ZDDP and ZDDP degradation products were also detected in the

final sooted and centrifuged samples, as shown in Figure 7c,d (both negative ion mode), respectively. A homologous series of reaction products formed by dipropyl dithiophosphate and salicylate detergents (m/z 599.300; 641.347; 689.394) as well as a similar product of sulfuric acid, a ZDDP degradation product, and salicylate (m/z 429.195), are shown. The presence of these structures highlights the complexity of FFOs and the (tribo)chemical reaction involved in engine oil degradation. Such chemical pathways are not available in fresh model lubricants common in the literature, e.g., [22,23], where only some of the common additives are considered and oil degradation is largely absent.

Soot Additive Binding

Figure 8a gives an overview of the elemental composition via EDX of the isolated and extracted soot samples from the final sooted oil, namely after three n-heptane washing steps and the solid residues after the subsequent 2-propanol and toluene extractions (see Section 2.2.1). The two solvents were selected based on their polarity, with 2-propanol being a moderately polar, while toluene is a strong apolar solvent. Accordingly, it was expected that a good overview of the organic structures present in the soot particles could be achieved, irrespective of the polarity of the species. The three soot samples display a similar elemental composition, where carbon and to a lesser extent oxygen are identified as the main components. The concentrations of the main components were in the range of 92.0–95.3 m% for carbon and 3.8–7.0 m% for oxygen, which correspond well to the composition reported by Clague et al. [29]. Additionally, oil additive elements, namely calcium, phosphorus, sulfur and zinc are also detectable as trace elements (<1 m%) in the soot samples. This indicates overall that ZDDP antiwear and calcium carbonate base reserve and/or their respective degradation products are also incorporated in the soot particles. These results are similar to investigations considering isolated crankcase soot samples by Thersleff et al. [16].

To better understand the additive binding on soot particles, HR-MS analysis of the 2-propanol and toluene extracts (liquids) was performed. The presented extracts were produced from isolated soot particles, which were washed three times with approx. 30 g n-heptane before the extraction; accordingly, contamination by the oil samples is very unlikely. The characterization of the 2-propanol and toluene soot extracts is given by a comparison to the fresh engine oil in Figure 8b–e. In detail, Figure 8b (positive ion mode) displays the identified aminic antioxidants (m/z 296.237 and 422.378). As shown, both aminic antioxidant structures were detectable in the soot extracts. Comparatively, the sulfonate detergents (m/z 437.310 and m/z 465.341) seemed to be more abundant in the 2-propanol extract, but they were also detectable in the toluene solution (Figure 8c (negative ion mode)). This was also true for further salicylate species as well ($C_{24}H_{49}$ alkyl sidechain, m/z 493.373). The salicylate detergents (m/z 333.234) displayed a comparable abundance in both extracts (Figure 8d) (negative ion mode). Figure 8e (negative ion mode) shows the degradation products of both ZDDP and phenolic antioxidants. The presented dihexyl thiophosphate (m/z 281.131) and dihexyl phosphate (m/z 265.155) are more abundant in the toluene extract. Furthermore, all discussed dialkyl thiophosphate and dialkyl phosphate species, namely dipropyl, propyl-hexyl, and dioctyl alkyl sidechains, were detected in both extracts. Additionally, further ZDDP degradation products, such as propyl phosphate (m/z 139.015) and propyl sulfate (m/z 139.006), were present in both extracts. The degraded phenolic antioxidants (m/z 277.181 and 291.197) are prevalent in the 2-propanol extract and to a lesser extent in the toluene extract as well. As these molecules result from the oxidation of the present phenolic antioxidants, various other, comparable configurations were also found, e.g., m/z 233.152, 305.212, and 389.306, mainly differing in the length and configuration of the alkyl sidechains present on the aromatic ring. The presence of these species gives us valuable insight into the applied phenolic antioxidant, which seems to be a sterically hindered phenol.

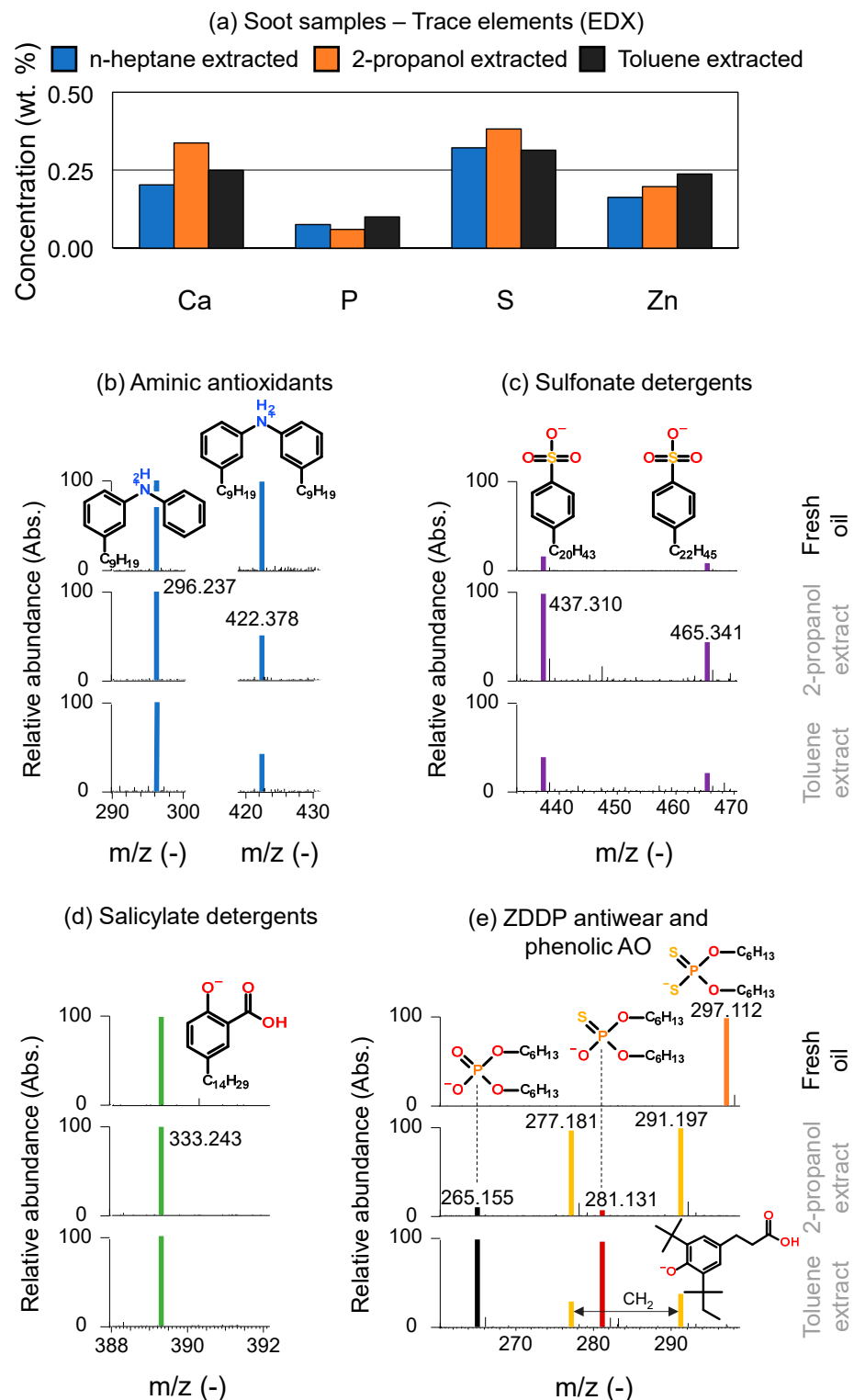


Figure 8. (a) Additive elements in the isolated soot samples identified via EDX; identified additives and degradation products in the soot extracts via HR-MS; (b) aminic AOs (positive ion mode); (c) sulfonate detergent (negative ion mode); (d) phenolic antioxidants (negative ion mode); (e) ZDDP and degradation products (negative ion mode).

Overall, comparison of Figures 6 and 8 shows that practically all relevant additives present in the fresh oil were bound to the soot particles to some extent. This reveals one of the possible negative impacts of soot during engine operation: when additives are bound

to the solid soot particles, they are no longer able to perform their intended functions in the engine oil. This might result in subpar lubrication performance (AW) and accelerated oil aging (AO).

3.3. Tribometrical Characterization—Results

Friction and wear are of key importance during the application of engine oils. To determine the impact of soot on the tribological properties, SRV[®] experiments on the fresh engine oil, selected sooted oils (10 h, 50 h and 100 h), and the corresponding centrifuged oils was performed. The presented values are averaged from three determinations per oil sample, with the error bars displaying ± 1 standard deviation (SD). Figure 9a,b give an overview of the CoF, in detail, with exemplary CoF curves and values averaged from 1000 s to 6000 s, respectively (excluding the running-in phase). The sooted oil samples show an increase in friction and more pronounced fluctuations, which can be attributed to the formation and subsequent breakdown of soot agglomerates. Ernesto et al. studied soot agglomerate building [50] and found that soot agglomeration can occur in sliding contacts. They reported that crescent-shaped soot agglomerates propagate in a (ball-on-disc) lubricated contact, while its shape, thickness, and soot content changes over time in each stroke [50]. Such dynamic changes, constant origination, and breakdown of soot agglomerates can very well explain the elevated fluctuation in the sooted oils compared to the fresh and centrifuged counterparts. Here, the average CoF increases from approx. 0.14 to approx. 0.16 during the 100 h of the engine dynamometer test. The increase of 0.02 in CoF is comparable to previous field studies, e.g., in [34] an increase from 0.135 to 0.150 was reported in a passenger car during 20,000 km of on-road utilization using the same SRV[®] test protocol. Comparatively, the centrifuged samples behaved similarly to the fresh engine oil, the average CoF returned to approx. 0.14, and the fluctuations disappeared once the soot particles were removed.

The wear scar area as well as wear volume of the SRV[®] balls and discs are presented in Figure 9c–f, respectively (please note that the determination of the wear properties was not possible on one of the SRV[®] balls in the case of the 100 h sooted sample due to extensive material loss; accordingly, the results of this sample are averaged from two determinations only). Soot seems to have a severe negative impact on the wear properties of the engine oil samples. Wear scar area increased dynamically with the soot loading both on the SRV[®] ball and disc, with the former displaying an over 700% increase and the latter displaying an over 300% increase compared to the fresh oil. Similarly, wear volume also increased drastically with the soot loading, even after 10 h of operation in the engine dynamometer, as an over 1100% increase on the ball and an over 350% increase on the disc are visible. This is even higher in the case of the final sooted sample, which is over 9000% on the ball and over 2500% on the disc. This increase is extraordinary, as it is almost two orders of magnitude in the case of the SRV[®] balls. Comparatively, the field test described in [34] reports a 420% increase in wear volume after 20,000 km of mileage in a conventional passenger car at the end of the lubricant's useful life.

Despite the severe increase in wear, this seems to be also reversible by the removal of the soot, similarly to the viscosity, density, and CoF. Both wear scar area and wear volume return to comparable levels to the fresh oil, even in the case of the 100 h centrifuged sample; accordingly, the diminished tribological properties can be directly attributed to the soot present in the engine oil samples. This corresponds well with the findings of the conventional and advanced oil analyses (see Sections 3.1 and 3.2, respectively), where only a minor degradation of the base oil and the oil additives was demonstrated. The physical properties, i.e., the viscosity and density, of the centrifuged oils are similar to the fresh oil; furthermore, a comparable elemental composition and high residual additive content were detected. Accordingly, there is no identifiable reason for the centrifuged samples to underperform the fresh lubricant once the soot is removed.

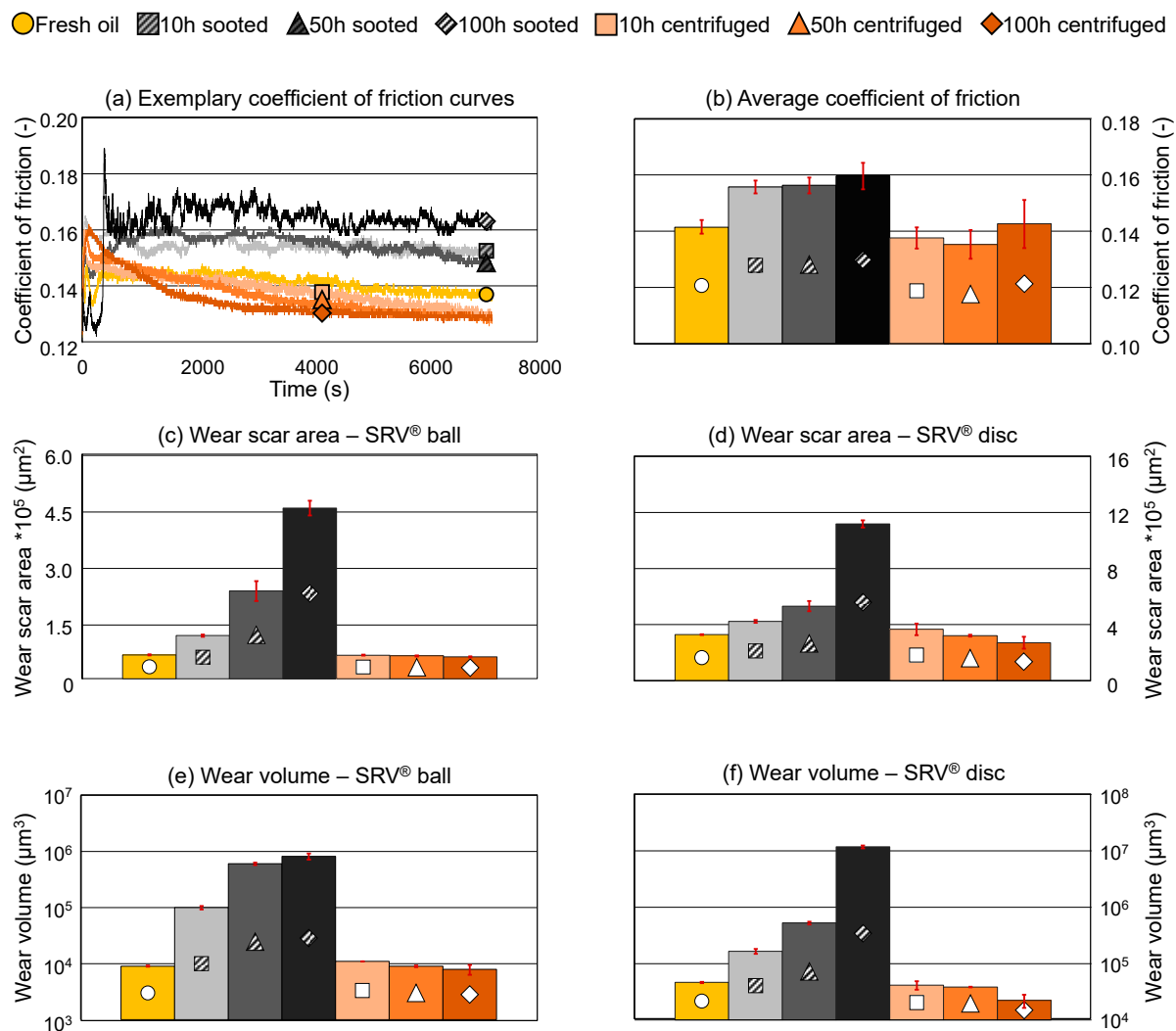


Figure 9. Friction and wear properties of the fresh, sooted, and centrifuged engine oil samples. (a) Exemplary CoF curves; (b) average CoF; (c) wear scar area on the SRV[®] ball; (d) wear scar area on the SRV[®] disc; (e) wear volume on the SRV[®] ball; (f) wear volume on the SRV[®] disc. All error bars correspond to ± 1 standard deviation.

3.4. Tribofilm Composition

To better understand the reasons behind the negative impact of soot on tribological properties, surface characterization of the SRV[®] discs was performed using XPS to study the present tribofilms. The tribofilms formed by ZDDP are well understood: glassy Fe/Zn polyphosphate “pads” are formed on a thin zinc sulfide/iron sulfide base layer [17]. A schematic representation of typical ZDDP tribofilms is given in Figure 10a, while the results of the performed single-spot scans are in Figure 10b–e.

The main components of all formed films are carbon and oxygen, where no significant differences can be seen between the samples, although the 100 h sooted oil generally displayed more carbon and less oxygen compared to the other samples. This might be due to the severe wear which occurred in the case of this sample. Figure 10b,c displays the concentration of iron, which is indicative of the substrate or wear particles, as well as calcium, which is indicative of the base reserve, respectively. As shown, the sooted oils formed films with significantly more iron and less calcium; accordingly, the incorporation of the base reserve into the tribofilm was also inhibited. Furthermore, the higher iron content either suggests lower surface coverage (more substrate is directly on the surface) or a higher concentration of wear particles on the surface. Once again, the changes occurring

in the case of the sooted oils dissipate once soot is removed from the oil samples, as the surface compositions of all centrifuged samples were very comparable to the fresh oil.

● Fresh oil ▨ 10h sooted ▲ 50h sooted ◆ 100h sooted ◻ 10h centrifuged ▲ 50h centrifuged ◆ 100h centrifuged

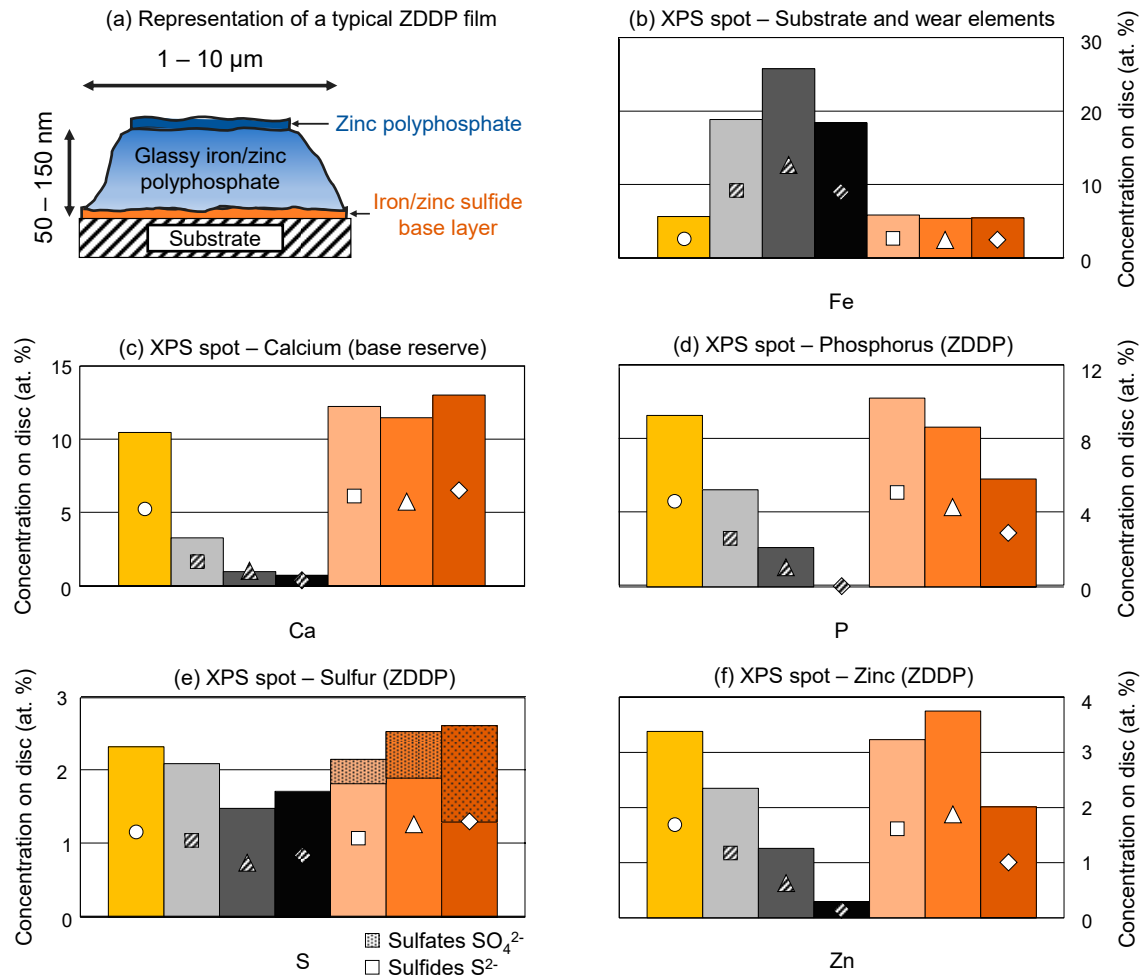


Figure 10. Tribofilm composition on the SRV® discs. (a) Schematic representation according to [17]; (b) iron; (c) calcium; (d) phosphor; (e) sulfur (sulfides and sulfates); (f) zinc.

Figure 10d displays phosphorus, indicative of a ZDDP tribofilm. As shown, phosphorus shows a diminishing concentration in the sooted oil samples with increasing soot loading (increasing utilization time), which is consistent with other surface composition results, e.g., [25,27]. In the case of the 100 h sample, phosphorus is not detectable on the surface, and the glassy polyphosphate film formation seems to be completely inhibited, despite ZDDP being present in this oil sample. The slightly decreasing concentration of phosphorus in the layers formed by the centrifuged oils corresponds well with the determined partial degradation of ZDDP, which was indicated by both FTIR and HR-MS (see Figures 3d and 6d). Comparatively, sulfur (Figure 10e) shows only a minor decrease in the sooted oils, and, overall, a low concentration, as this element is mostly present in the thin base layer [17]. Here a further observation can be made: when looking at the abundance of both sulfates (SO_4^{2-}) as well as sulfides (S^{2-}), the amount of sulfates shows an increasing trend in the centrifuged oils, while sulfates are not present in the fresh and sooted samples. The tribofilm composition of the centrifuged oils corresponds well with previous results of Dörr et al., who reported a decreasing sulfide/sulfate ratio in the tribofilm as ZDDP degradation progressed [32], and with the phosphorus results, and also highlights the impact of the initial degradation of ZDDP during the engine dynamometer test.

Furthermore, another important observation can be made, namely that the concentration of sulfides is very similar in all of the oil samples, including all the sooted oil samples. It seems that soot has practically no influence on sulfide film formation (base layer) and only affects the sulfates and glassy polyphosphates deposited on top of the initial film on the substrate surface. This is largely consistent with the tribocorrosion-based model of wear in sooted oils, where it is suggested that the sulfide base layer can form rapidly on the metal surface [23], but it is rapidly removed by the soot particles, as further layers of the tribofilm cannot form. The zinc concentration in the tribofilms is displayed in Figure 3e. The total zinc concentration in the tribofilm shows a steady decrease in the sooted oils, while the centrifuged and fresh lubricants once again form a similar surface layer. Some decrease is visible with the 100 h centrifuged oil, once again corresponding to the partial degradation of ZDDP.

The results are overall similar to field studies under real driving conditions. In [34], it was demonstrated that used oils form tribofilms with lower calcium, phosphorus, and zinc content, while the concentration of iron increases. Furthermore, it was also shown that fresh oils form films largely containing sulfides, while as ZDDP degradation progresses, sulfates become more dominant [32]. Accordingly, it seems that the engine dynamometer test results in very similar degradation and subsequent film formation to the real utilization case of most ICEs. Additionally, it was shown that both the wear rate and the tribofilm composition becomes similar to the fresh oil once soot is removed via ultracentrifugation. In [34], it was reported that the tribofilm composition suddenly changes and the wear rate increases once all dialkyl dithiophosphates and dialkyl thiophosphates are consumed. This was not the case for the sooted oils, as both dialkyl dithiophosphates as well as dialkyl thiophosphates are largely present after 100 h (Figures 6d and 7). Hence, ZDDP films are able to form in all centrifuged oils, which also matches the wear results presented in Figure 9. Once soot is removed from the oil samples via centrifugation, glassy polyphosphate film formation is no longer inhibited, and wear properties return to comparable levels to those of the fresh oil.

Further characterization of the tribofilms was performed by depth profile analysis and by mapping of the surfaces of the SRV[®] discs after testing with the fresh oil, as well as the 50 h sooted and centrifuged samples. These oils were selected as wear was severe in the case of the 100 h sooted oil and practically no tribofilm formed (see Figures 9d and 10a); hence, no useful information could be extracted from the surface. Figure 11a,b displays the depth profiles of the SRV[®] discs, measured in the middle of the wear scar, for iron and calcium, respectively. These results are used to estimate the tribofilm thickness of the various oil samples. For this purpose, iron and calcium were selected. The measurement of iron is comparatively accurate via XPS due to the relatively large nucleus, indicated by the large atomic number ($Z = 26$). This offers a large cross-section between the exciting X-Rays and the analyte; accordingly, the photoelectron emission (hence, the measured signal) is strong. Similarly, calcium also has a larger nucleus ($Z = 20$), and it is present at the highest concentration in the tribofilms (>18 at.%) among the additive elements. Comparatively, the measurement via zinc ($Z = 30$) is limited by its low concentration in the tribofilm (<4 at.%), phosphorus by the low atomic number ($Z = 15$), and sulfur by both factors ($Z = 16$; <3 at.%). In the case of iron, where a low signal is indicative of high surface coverage, the 50 h sooted oil is almost indistinguishable from a clean substrate (blank), which shows that tribofilm formation was severely limited. The 10 h sooted sample displays some coverage, as the iron concentration is lower than the substrate until approx. 40 nm, but the overall trend is rather similar to the 50 h sooted oil. Comparatively, all three centrifuged samples behave very similarly to the fresh oil. The surface is completely covered, and the estimated film thickness lays in the range of 50–60 nm, where the fresh and centrifuged samples became similar to the substrate. The measurement performed by the calcium content shows a very comparable picture: the 50 h sooted sample is very close to the substrate, the 10 h sooted oil shows some film formation until approx. 30 nm, and the fresh and centrifuged samples display an estimated film thickness of 50–60 nm. Generally, both elements show similar film thickness for all samples; accordingly, it can be assumed that the performed estimate is

relatively accurate: The estimated 50–60 nm value in the cases of the fresh and centrifuged samples lies within the range of the typical film thickness of 50–150 nm reported in the literature [17].

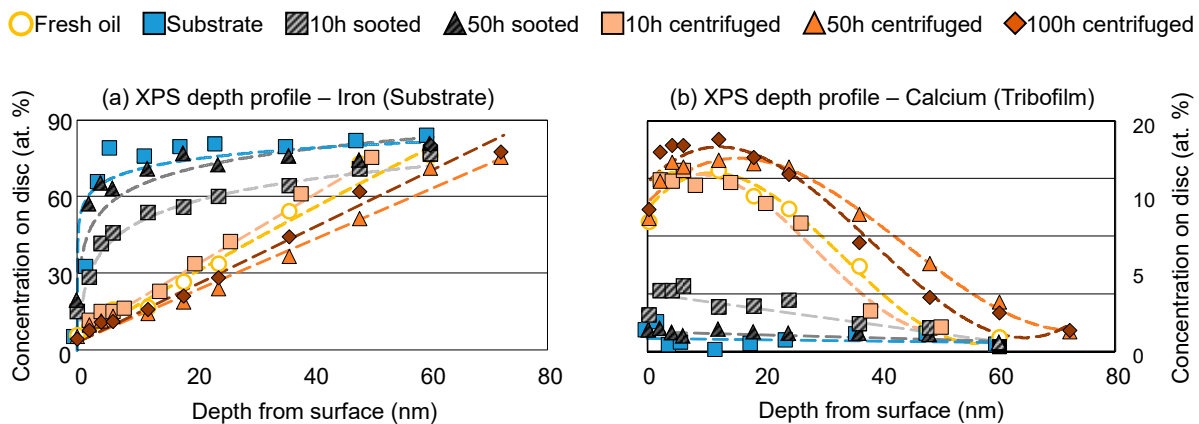


Figure 11. XPS depth profiles of selected sooted and centrifuged samples—tribofilm thickness estimation. (a) Iron (substrate); (b): calcium (base reserve additive in tribofilm).

Figure 12a,b shows the wear scars and the 3D surface topography of selected samples on the SRV[®] discs, respectively. The 50 h sooted oil sample produced a comparatively large wear scar, where deep scratches on the surface parallel to the direction of movement are prevalent, which is indicative of abrasive wear [19,51]. An abrasive wear mechanism in case of high soot loading is often suggested in the literature as well [18,19,47]. The scratches reach over 1 μm deep in the center of the wear scar. The fresh oil and the 50 h centrifuged sample show a better and comparable surface quality: the wear scars are generally smaller than in case of the 50 h centrifuged sample, and are significantly less deep as well. This is all reflected in the evaluation of the wear scar area and wear volume in Figure 9d,e, respectively.

The corresponding surface maps are presented in Figure 12c–i. As shown, the fresh oil forms a uniform tribofilm, where the film composition shows no variation along the wear scar. This consists of calcium (c), phosphor (d), which is present as organic phosphates (e), low levels of sulfides (f), and zinc (g), i.e., a typical ZDDP tribofilm. Comparatively, the named additive elements are almost completely missing from the surface in the case of the 50 h sooted oil, and only low levels of organic phosphates (in the boundary region) and sulfides are detectable. It is notable that the sooted oil shows a higher sulfide concentration on the surface compared to the fresh and centrifuged samples, especially at the reversal points. Sulfides are not expected to be detectable in the cases of the fresh and centrifuged samples, as sulfides form the base layer directly on the metal substrate (see Figure 10a), so they are covered if a glassy polyphosphate layer is also deposited. This was the case when no soot was present. The presence of sulfides on the surface in the case of the sooted oil sample is consistent with the results of the spot measurements (see Figure 10e) and the tribocorrosion-based wear interpretation of Kontou et al. [23], as they theorized that an iron sulfide film (tribofilm base layer) can form when soot is present, but that this is subsequently quickly removed by the particles in an abrasive manner. As the surface in the case of the 50 h sooted oil shows a sulfide layer, it can be concluded that a sulfide film can indeed be deposited in sooted oils. Meanwhile, no organic phosphates are visible in this case, which once again shows that the formation of the glassy polyphosphate protective layer is inhibited by soot, and only becomes viable once again once the soot is removed from the lubricant. The 50 h centrifuged sample is once again comparable to the fresh oil, as additive elements are largely present on the surface everywhere, in similar concentrations, and only minor inhomogeneities are observable. This corresponds to the already presented findings of wear properties, where the fresh oil and the 50 h centrifuged sample showed very comparable behavior in terms of wear scar area and wear volume.

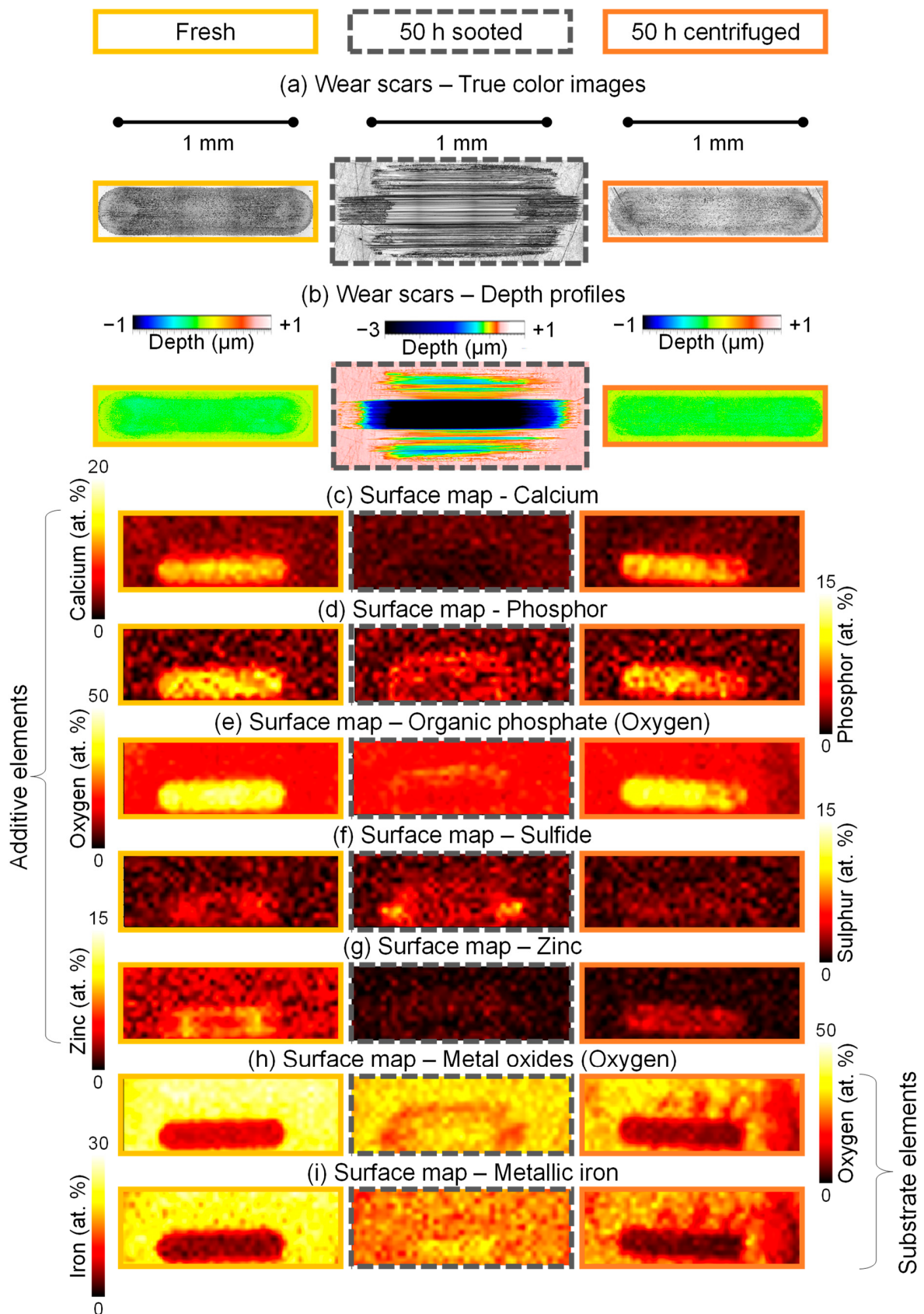


Figure 12. Wear scars and surface maps of the fresh, 50 h sooted, and 50 h centrifuged oils. (a) True color images; (b) surface topography; (c) calcium; (d) phosphor; (e) organic phosphates; (f) sulfides; (g) zinc, (h) metal oxides; (i) metallic iron.

Analysis of the substrate elements, namely metal oxides and metallic iron, is displayed in Figure 12h–i. The substrate surface maps show a comparable picture to the additive elements: the fresh oil and the 50 h centrifuged samples are largely similar, while the 50 h sooted oil differs significantly. Both metal oxides and metallic iron show a lower concentration in the wear scar than the surrounding surface in the case of the fresh and centrifuged samples, indicated by dark “tracks”. Comparatively, the wear scar is barely distinguishable from the disc surface in the case of the sooted oil sample, indicating that the surface is mostly not covered, and the substrate is showing. Some film formation (surface coverage) is visible, but only in some selected areas, i.e., “patches”, and the distribution is not uniform.

To summarize, the surface maps corroborate the findings of the single-spot XPS analysis on the whole tribologically active surfaces. The fresh and 50 h centrifuged oil samples are able to form uniform ZDDP tribofilms, while film formation of glassy polyphosphates is completely inhibited in the case of the 50 h sooted oil, but the presence of a sulfide base layer was confirmed. The soot particles abrasively remove this sulfide base layer, which subsequently leads to significantly increased tribocorrosion-mediated wear of the surface. However, this phenomenon is completely reversible via the removal of the soot particles from the oil samples, as additives are still present to a greater extent and the overall oil degradation is not severe.

4. Summary and Conclusions

An engine dynamometer test was conducted based on ASTM D7484 [35] for 100 h, where injection timing was retarded to promote soot formation. Soot was removed from the oil samples via ultracentrifugation, and analyses and comparisons of both sooted and centrifuged oils were then conducted. After a 100 h dynamometer run, the sooted oils displayed the following attributes:

- Mild degradation (high residual AOs and ZDDP).
- Low levels of oxidation and nitration products.
- Minor NN increase and TBN decrease.
- Increasing kinematic viscosity and shear-rate dependency.
- No major changes in additive elements.
- A strong accumulation of iron, indicative of engine wear (approx. 10,000 km in on-rad diesel engines).
- The changes in the physical properties were completely reversible, once soot was removed from the oil samples.

HR-MS confirmed the initial degradation of the oil samples on a molecular level. Some degradation of ZDDP was visible, but additives were not completely depleted.

Tribometrical characterization via SRV[®] showed an increase in friction and wear, namely over 9000% on the ball and over 2500% on the disc for the final sooted sample, which can be seen as severe. Despite this drastic increase, the centrifuged samples performed comparably to the fresh oil; accordingly, the impact on tribological performance was also reversible by the removal of soot, similarly to the physical properties. This also showed that additive binding on soot played a minor role at this early stage of the oil degradation compared to the presence of soot particles; however, it is possible that the adsorption of additives might have a higher impact once oil degradation progresses and the additives are largely consumed.

Surface characterization revealed decreasing calcium, phosphor, and zinc in the tribofilms formed by sooted oils, while centrifuged samples produced similar tribofilms to the fresh oil. This shows that glassy polyphosphate film formation once again becomes possible once soot is removed from the lubricants. Comparatively, a close-to-constant total sulfur concentration of the tribofilms was observed in all cases. The fresh and sooted oil films contained sulfur only as sulfides, while in the films of the centrifuged oils, an increasing abundance of sulfates was detected. The presence of sulfates in the centrifuged oil can be attributed to the early stages of ZDDP degradation [32], but the absence of sulfates in the

sooted oils is more interesting. This result shows that the formation of sulfide films, which are commonly considered as the base layer of ZDDP films, is not inhibited by soot, and that only the subsequent deposition of the polyphosphate pads is affected. These observations were also confirmed by the mapping of the whole surface of selected discs, where a uniform phosphate film was found in the case of the fresh and centrifuged oil; meanwhile the sooted oil formed a thin layer mainly consisting of sulfides only, which was especially present in the reversal points of the tribotrack.

These results suggest that a tribocorrosion-based wear mechanism is responsible for the increased wear. In detail, the iron sulfide base layer of the ZDDP tribofilm can form in sooted oils, but the subsequent deposition of the iron/zinc polyphosphate pads, which are largely responsible for the wear protection, is inhibited. The iron sulfide layer is removed at a high rate through abrasive wear, as its hardness is low compared to the steel substrate. Since the iron sulfide layer formation is not inhibited, it reforms continuously, using up the substrate, which results in elevated wear rates. Figure 13 shows the schematic representation of this theorized tribocorrosion-based wear mechanism. Furthermore, this also helps to explain why an increased wear in sooted FFOs is observable compared to sooted base oils [22,24]: in BOs, no iron sulfide film formation is possible (as there is no ZDDP present); accordingly, the soot particles interact with the much harder substrate surface directly, resulting in lower wear rates. These results and the given interpretation are largely consistent with literature on model lubricants containing carbon black as a soot surrogate [23] and show that the proposed wear mechanism is detectable in commercially available lubricants operating in an ICE, even when contaminated by real crankcase soot. However, it has to be mentioned that both additive binding to soot particles as well as three-body abrasion in the tribological contact were also indicated to some degree, although these effects seem less dominant factors in the wear increase.

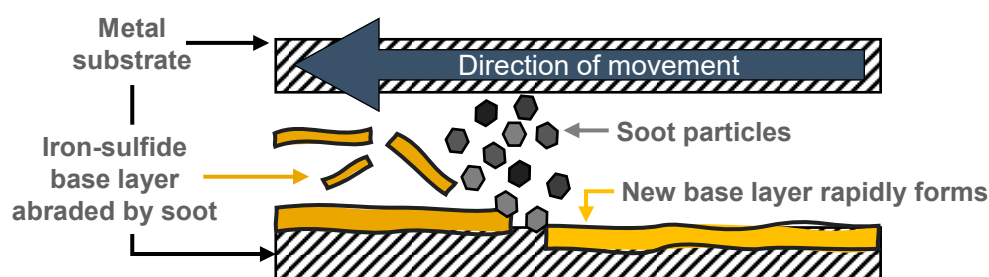


Figure 13. Schematic representation of the theorized tribocorrosion-based wear mechanism of soot.

Additionally, it must be mentioned that the presented results indicate the possibility of extending the useful life of engine oils by utilizing better soot removal. This is most likely impractical for on-road utilization, especially for passenger cars [19], due to space constraints and the relatively low cost of an oil change. However, soot removal is conceivable for large engines, such as in the cases of power generation, rail, or marine applications, where CI engines are commonly utilized. As both friction and wear in the centrifuged oils returned to comparable levels to the fresh lubricant, the application of, e.g., centrifugal filters or other soot removal systems, would likely result in similar results. Some patented strategies for this purpose involve the utilization of electrical fields [52] or heterogeneous strong bases [53]. In general, soot removal allows the extension of an engine's lifetime through a reduction in wear and oil change intervals as well, which offers reliability, cost, and overall emission benefits. Accordingly, the application of such systems could be considered, where space constraints allow it; however, a cost-benefit analysis is necessary in each case to determine commercial viability. A possible further or complementary wear reduction strategy could be the utilization of friction modifiers (FMs) in the fuel. A recent study from Frauscher et al. showed that adding FMs in the fuel can strongly reduce the wear of piston rings, even when FMs and AW additives are completely depleted [54];

however, the interactions between soot and FMs in the piston ring–cylinder liner contact must be analyzed in detail in future work.

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