



Article Characterization of Base Oil and Additive Oxidation Products from Formulated Lubricant by Ultra-High Resolution Mass Spectrometry

Oscar Lacroix-Andrivet ^{1,2,3}, Marie Hubert-Roux ^{2,3}, Corinne Loutelier Bourhis ², Samira Moualdi ¹, Anna Luiza Mendes Siqueira ^{1,2} and Carlos Afonso ^{2,3,*}

- ¹ TotalEnergies OneTech R&D, Centre de Recherche de Solaize (CRES), Chemin Du Canal, BP 22, 69360 Solaize, France; oscar.lacroix-andrivet@external.totalenergies.com (O.L.-A.); anna-luiza.mendes-siqueira@totalenergies.com (A.L.M.S.)
- ² INSA Rouen Normandie, CNRS, University Rouen Normandie, Normandie University, COBRA UMR 6014, INC3M FR 3038, 76000 Rouen, France; marie.hubert@univ-rouen.fr (M.H.-R.); corring loutelier@univ-rouen fr (C.L.B.)
- ³ International Joint Laboratory—iC2MC: Complex Matrices Molecular Characterization, TRTG, BP 27, 76700 Harfleur, France
- * Correspondence: carlos.afonso@univ-rouen.fr

Abstract: Automotive formulated lubricants are high value products composed of 80% base oil and 20% various additives. During their life service, lubricants are exposed to several factors that will cause degradation over time, such as high temperature, shear, and oxidation. Base oil is a complex combination of hydrocarbons that are relatively sensitive to oxidation. During the initiation phase of oxidation, free radicals are formed, leading to the production of hydroperoxide ROOH and an alkyl radical R[•]. These compounds will react with the base oil molecules to form aldehydes, ketones, and carboxylic acids in the termination phase. Owing to the molecular complexity of these mixtures, Fourier transform mass spectrometry seems to be the most appropriate tool to cover their wide range of compounds due to its ultra-high resolving power and mass accuracy. In this study, a native formulated lubricant and its different oxidized states at 140 °C under air flow (3, 5, 7, 8, and 9 days of oxidation) were analyzed by FTICR MS. The combination of atmospheric pressure chemical ionization (APCI) was used to achieve a non-selective ionization of molecules, including base oils, while Electrospray ionization (ESI) was used to selectively ionize acidic molecules. Apparent Kendrick mass defect (aKMD) plots were used to separate homologous series of molecules on different horizontal lines on the basis of the CH₂ repetition unit. Aging of lubricants was mainly characterized by a rapid consumption of certain additive families, such as molybdenum dithiocarbamates (MoDTCs) and zinc dithiophosphate (ZnDTPs), but also by the emergence of many oxidation products. Thus, the presence of aldehydes, ketones, and acids was characterized in the early stage of aging while larger products from polymerization were observed in a more advanced stage of aging. Interaction products between peroxy radicals and hindered phenols/alkyl diphenylamines (ADPAs) antioxidations were elucidated toward the high m/z. The formation of such products can be explained by trapping mechanisms of these additives at high temperature (>120 °C). Other types of interaction products were observed with the formation of antioxidant complexes. Additive degradation products were also characterized. For instance, polyisobutenyl succinimide dispersant oxidation products were clearly evidenced on the aKMD plots due to the gaps of 56 Da between each point. Overall, this study demonstrated the efficiency of the aKMD approach, and the use of ESI/APCI to characterize base oil and additive oxidation products.

Keywords: lubricant additives; aging; mass spectrometry; FTICR; Kendrick mass defect



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1. Introduction

The progressive development of engines has led to more demanding operating conditions, including longer oil change periods. Although oils are subject to new refining methods, it is necessary to improve their performance by adding various additives. Thus, lubricating oil manufacturers evaluate the performance of base oils and additives to produce the best performance/cost ratio. The ready-to-market product is composed of about 80% base oil and about 20% additives, but this ratio can vary depending on the manufacturer and the intended application [1]. The additives are generally low molecular weight polymeric molecules with a wide range of chemical functions, with compounds containing oxygen, nitrogen, sulfur, phosphorus, boron, and molybdenum. These additives can be classified as dispersants, detergents, antioxidants, anti-wear agents, viscosity modifiers, and friction modifiers [2–6]. The formulated lubricant is used to reduce friction and wear to increase the service life of the engine in case of automotive application. Oils are then exposed to several factors that will cause degradation over time, such as high temperature, shear, and oxidation [7]. Degradation products are mainly obtained by the oxidation of base oil, particularly with mineral base oil. Indeed, the composition of a mineral base oil is a complex combination of hydrocarbons, primarily paraffinic and naphthenic, with a small proportion of nitrogen and sulfur-containing compounds. These hydrocarbons are relatively sensitive to oxidative deterioration, and their sensitivities will greatly depend on the origin of the crude oil [8]. For instance, oils with a high alkyl-substituted aromatic content are very sensitive to oxidation, forming organic acids that will generate soot. Base oils with a high paraffinic content will be oxidized more slowly, forming weak acids. The rate of oxidation of oils will be mainly impacted by the abundance of oxygen and by the increase in temperature [9]. At the macroscopic level, oxidation will result in a darkening and thickening of oils, which reduces their performance. Oxidation can be described in three distinct phases. During the initiation phase, free radicals are produced from base oil molecules. The formation of these products is greatly accelerated by the presence of transition metals coming from the friction between the metal parts of the engine, which will react with oxygen to form HOO[•] radicals [10]. A propagation phase will then take place with the formation of peroxide radicals ROO[•], which will randomly pull the proton of a hydrocarbon to form a hydroperoxide ROOH and an alkyl radical R[•]. These compounds can react with the base oil molecules to form acidic compounds, and this is called the termination phase. The main oxidation products of base oils were described in the literature as alcohols, aldehydes, ketones, and carboxylic acids [11]. These products correspond to primary oxidation phase products. In the case of a high concentration of oxidation products, the increase in acidity is clearly corrosive to the engine components and will form metal ion carboxylates (soaps). At high temperature (>120 °C), these acidic compounds will then polymerize and form secondary oxidation phase products with higher molecular weight molecules, which will eventually lead to the formation of soot and deposits [12,13]. Overall, the increase in viscosity will lead to wearing of the rubbing part of the engine, a decrease in low temperature properties, and difficultly in starting the engine [14].

Several studies of lubricant oil oxidation were reported in the literature. For instance, Obiols used the FTIR analytical peak area increase (PAI) method combined with viscosity analyses to characterize the degradation of lubricants [15]. Two phases of oxidation were described. The first one corresponded to the initiation period, in which lubricant is protected by its antioxidants, and the oxidation of certain polymers led to a reduction of their thickening power and to a slight decrease in the viscosity index (VI). The second phase displayed a sudden degradation phase of the lubricants' physicochemical properties with the production of a large quantity of carbonyl compounds, which yielded an increase in molecular weight, thickening, and a loss of VI. El-Naggar et al. used a combination of standard test procedures (total acid number, flash point, viscosity, sludge content, and carbon residue) with capillary gas chromatography to evaluate the quality of light as well as medium and heavy mineral base oils [11]. They demonstrated that the thermal stability of base oils decreased with the heaviest oil. Heavy oil displayed the lowest percentages of

paraffinic hydrocarbons compared to light and middle ones. These studies corresponded to bulk-resolution analytical methods, yielding information on the overall behavior of the studied oils, with information on the physicochemical properties and the chemical functions. Lavison-Bompard et al. carried out a feasibility study of a hypernated SFC system, including FID, UV, FTIR, AED, and MS, for native and used car lubricant analysis. This study describes the identification and the elucidation of the structure of selected additives in a formulated lubricant, but at present, the system has not been implemented to reach the full detailed analysis of its constituents [16]. Characterization of oxidation products at the molecular level could allow us to obtain a better understanding of oil oxidation and additive degradation mechanisms. Indeed, this makes it possible to study each mechanism independently due to molecular formulas that can be assigned to each of the species identified on the mass spectrum.

Characterization of oxidation products at the molecular level could allow us to obtain a better understanding of oil oxidation and additive degradation mechanisms.

At the molecular level, mass spectrometry hyphenated or not hyphenated to separation methods, such as chromatography or ion mobility spectrometry, was largely used for the characterization of lubricant additives [17–23]. Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) is the best instrument to characterize complex organic mixtures at the molecular level [24,25]. The ultra-high resolution and mass accuracy of FTICR allow us to attribute a molecular formula to each ion unambiguously. Furthermore, determination of the isotopic fine structure (IFS) of the ions is especially required in the case of formulated lubricant in order to unambiguously attribute molecular formulas to compounds that are rich in heteroelements and metals, and, therefore, avoid miss assignments [26]. The access to IFS requires very high resolution and dynamic range, which are only possible with high field FTICR instruments [27]. FTICR MS was already used to characterize base oils at the molecular level with atmospheric pressure photo ionization (APPI) and APCI sources [28,29]. In a previous study, combination of atmospheric pressure chemical ionization (APCI) and electrospray ionization sources was used to gain an exhaustive characterization of formulated lubricants. APCI in positive ion mode allowed a non-selective ionization of low polar, polar, and aromatic species, including base oil molecules, while ESI in negative ion mode allowed a selective ionization of acid molecules, including, for instance, sulfonate detergents. Data were plotted according to their apparent mass defect with apparent Kendrick mass defect (aKMD) plots [30,31], which allowed specific aKMD values for each additive family to be obtained, which could thus be implemented in a database.

In this study, a combination of non-selective APCI(+) and selective ESI(-) ionization sources in direct infusion was used to characterize a native and laboratory-aged formulated lubricant sample. Several aging times were studied in order to determine the aging kinetics of this mixture. The aim was to elucidate the degradation products of the various additives as well as the base oil oxidation products at the molecular level. To our knowledge, the characterization of oxidized formulated lubricants at the molecular level has never been described in the literature. The elucidation of the molecular formulas allowed a deeper understanding of the degradation mechanism of additives and their lifetime in order to prevent oxidation of the base oil.

2. Materials and Methods

2.1. Sample Preparation

Samples were obtained from TotalEnergies OneTech. The native formulated lubricant corresponds to an automotive lubricant containing an additive package at approximately 20% in mass quantity. In addition to the native sample (NL), 5 aging durations were obtained with 3, 5, 7, 8, and 9 days of aging (AL-3d, AL-5d, AL-7d, AL-8d, and AL-9d). The sample list was listed in Table 1. The aging procedure corresponds to an artificial laboratory aging process based on a published work, with an oxidation of the samples under heating and constant air flow [32]. For direct infusion FTICR-MS analyses, samples

were solubilized in n-heptane (C7) at 0.1 mg mL⁻¹ for APCI. For ESI, solutions were prepared in toluene/methanol mixture (50/50, v/v) at 0.05 mg mL⁻¹, with the addition of 3% of ammonium hydroxide solution (30% of NH₄OH in H₂O). A picture of the stock solutions solubilize in toluene was presented in Figure S1.

Table 1. Sample list.

Samples	Aging DURATION (Day)	
NL (native lubricant)	0	
AL-3d (aged lubricant)	3	
AL-5d (aged lubricant)	5	
AL-7d (aged lubricant)	7	
AL-8d (aged lubricant)	8	
AL-9d (aged lubricant)	9	

2.2. FTICR MS Analyses

FTICR MS analyses were carried out with a Bruker Solarix XR instrument equipped with a 12 T superconducting magnet and a dynamically harmonized ICR cell (ParacellTM). ESI and APCI ionization sources correspond to the commercially available sources from Bruker. Source, ion transfer, and acquisition parameters for both sources are listed in Table 2.

Table 2. FTICR parameters used with APCI and ESI ionization sources for the NL and AL sample analyses.

		APCI(+)	ESI(-)
Source	Flow (μ L h ⁻¹)	600	600
	Nebulizer gas pressure (bar)	2.0	1.0
	Drying flow ($L \min^{-1}$)	2.0	4.0
	Drying temperature (°C)	200	200
	Vaporization temperature (°C)	300	-
	Corona needle (knA)	4.0	-
Ion transfer	Capillary voltage (kV)	-4.5	3.9
	Quadrupole m/z	150	150
	Time of flight (ms)	0.7	0.8
Acquisition	m/z range	202.7-1300	147-1000
	Scan number	200	200
	Accumulation time (s)	0.1	0.035
	Transient length (s)	3.35	1.67

The analogue image current was digitized with 8 million data points, resulting in the recording of a 3.34 s time domain signal for APCI analyses, and 4 million data points resulting in the recording of a 1.67 s time domain signal for ESI analyses. These time domain signals were transformed into the corresponding frequency domain by Fourier transform (one zero fill and full-sine apodization). These settings result in a mass spectrometric resolving power of 650,000 at m/z 400. The dynamically harmonized cell (ParacellTM) was tuned following a published procedure [33]. Molecular formulas were assigned to the peaks with a signal-to-noise ratio (S/N) greater than 3, with even electron configuration allowed for ESI(-) and odd plus even electron configurations allowed for APCI(+). Tandem mass spectrometry analyses were carried out using collision-induced dissociation (CID) in order to obtain fragments of the desire ion precursor [34–36]. This technique consists of the acceleration of the ions previously filtered by the quadrupole into a collision cell filled with a neutral gas (argon or nitrogen). The level of fragmentation depends on several parameters, such as the pressure, the nature of the gas, and the acceleration voltage that is applied [37]. The resulting fragments are then detected in the ICR cell. For a nominal mass fragmentation, a window of one Dalton is set to isolate as few peaks as possible.

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2.3. Data Processing

FTICR data were processed with Data Analysis 5.0 software (Bruker, Billerica, MA, USA). Each mass spectrum was internally calibrated using confident ions signals present over the whole mass range. Molecular formula assignment of the whole mass spectrum was carried out in sequential mode using an exclusion mass list. This means that when a molecular formula was assigned to an m/z ratio, it was then removed from the mass list to not be reassigned. This allowed a stepwise assignment of the chemical family in an ascending order of complexity. In an on series, the most intense ion was manually controlled, checking, in particular, a good agreement with the experimental and theorical isotopic fine structure. Attribution of less intense ions was based on their KMD (vide infra). After molecular formula assignments, typical error distributions were found below 400 ppb.

Assigned formulas were processed with pyC2MC [38] and OriginPro (OriginLab, Barangaroo, Australia) softwares. For the apparent Kendrick mass defect plots, the KMD of molecules were calculated using the classical CH₂ base unit to obtain the Kendrick masses (KM) using the following equations:

Kendrick mass (KM) = observed IUPAC mass ×
$$\frac{\text{nominal mass of CH}_2(14)}{\text{IUPAC mass of CH}_2(14.01565)}$$
 (1)

Apparent nominal Kendrick mass (aNKM) = round (KM) (2)

Apparent Kendrick mass defect (aKMD) = aNKM - KM (3)

The nominal Kendrick mass corresponds to the Kendrick mass rounded to the nearest integer. In a general point of view, the determination of the nominal mass requires knowledge of the molecular formula. Here, the mass KM is rounded to the nearest integer, which does not necessarily correspond to the actual nominal mass. For KMD plots using the exact mass of ions after the assignation of molecular formulas, oxygen numbers were used as a color scale and relative intensities were used as a size scale.

3. Results and Discussion

3.1. Atmospheric Pressure Chemical Ionization Analysis

Figure 1 displays the APCI(+) mass spectra of the native and the five aged lubricant samples. The native lubricant sample (NL) in Figure 1a presented a very singular mass distribution compared to the aged lubricants (AL). Mass spectrum of NL was defined by very intense peaks corresponding to additives that overwhelm other signals. For instance, the major peak at m/z 422.37 corresponded to $[C_{30}H_{47}N + H]^+$ ion, which is an alkyl diphenylamine (ADPA) with C9 alkyl chains. It corresponds to radical scavenger antioxidant properties that act on peroxide radicals in order to prevent the propagation of the free radical chain during oil oxidation [39]. To observe other signals in the higher mass range, an enlargement between m/z 600 and 1100 was also plotted in Figure 1a. This allowed the presence of many ions that were covered by the high intensity of the major signals to be highlighted. Thus, very distinctive isotopic distributions were noticed at m/z922.17 and 1062.33. These m/z ratios were attributed to molybdenum dithiocarbamate (MoDTC) with $[C_{34}H_{68}Mo_2N_2O_2S_6 + H]^+$ and $[C_{44}H_{88}Mo_2N_2O_2S_6 + H]^+$ ions. MoDTC are indeed widely described friction modifier additives that present an extremely good tribological performance [40]. Aged lubricant samples evidenced a very dramatic change in the sample composition. As a matter of fact, none of the major signals of NL were found in the first state of the aging AL-3d (Figure 1b). Aged lubricant mass distributions can be defined as Gaussian distributions with major ions between m/z 300 and 600. The major ion in AL-3d at m/z 450.37305 matched with $[C_{31}H_{47}NO + H]^+$ ion, which seemed to correspond to an oxidation product of the ADPA described above. Although mass distributions of the AL samples looked quite similar, differences could be observed toward

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the high mass range (m/z > 600). Indeed, very intense ions were characterized in AL-3d with, for instance, an ion at m/z 806.64, which appeared to decrease for higher aging times. Overall, an increasing of complexity in terms of the number of ions with aging was evidenced by investigating these mass spectra.



Figure 1. APCI(+) broadband mass spectra of native and aged lubricants with: (**a**) native lubricant (NL), (**b**) AL-3d, (**c**) AL-5d, (**d**) AL-7d, (**e**) AL-8d, and (**f**) AL-9d.

3.2. Electrospray Ionization Analysis

Mass spectra obtained by ESI(–) for NL, AL-3d, and AL-9d were presented in Figure 2. As observed in APCI, major changes in the sample composition can be evidenced between the native and the aged lubricants. The major signal in the NL (Figure 2a) corresponded to a phenolic antioxidant $[C_{25}H_{42}O_3 - H]^-$ ion at m/z 389.30. This ion displayed a tremendous decrease in intensity in both of the AL samples. The major signal of AL-3d (Figure 2b) at m/z 293.17 seemed to fit with another form of phenolic antioxidant with $[C_{17}H_{26}O_4 - H]^-$ ion. This compound was consistent with an oxidation product of the ion at m/z 389.30. However, the ion at m/z 293.17 was also characterized on the NL sample at low abundance, so it cannot be ruled out that this compound also corresponds with a native additive. The mass spectrum of AL-9d can be defined as Gaussian distribution highlighting, as for APCI, that there is a very large increase in the complexity of the sample in the number of detected compounds in aged lubricants.



Figure 2. ESI(–) broadband mass spectra of native and aged lubricants with: (**a**) native lubricant (NL), (**b**) AL-3d, and (**c**) AL-9d.

3.3. Native Lubricant Characterizations

To have a general view of the lubricant composition, apparent KMD (aKMD) plots of APCI(+) and ESI(-) data were plotted in Figure 3. The use of this plot to characterize formulated lubricant was described in a previous study [31]. The terms apparent "Kendrick nominal mass" (aKNM) and "aKMD" were used, since a different definition of nominal masses than the IUPAC definition was used for the calculations. This can then explain the presence of negative aKMD values of several additive families on Figure 3a. These plots allowed the separation of the homologous series of molecules on different horizontal lines on the basis of the CH₂ repetition unit [30,41]. Additive families were well separated due to their specific aKMD values coupled to the use of a colormap based on the number of the oxygen atom. On the aKMD plot obtained with APCI data (Figure 3a), three additive families were observed in negative aKMD values. The first one at aKMD -0.145corresponded to MoDTC ($Mo_2N_2O_2S_6$) ions that were found at the highest masses. The second one at aKMD -0.379 corresponded to flame retardant additives (O₈P₂ and O₇P₂), as described in a recent patent [42]. The last additive family found on negative aKMD values at -0.422 corresponded to the multifunction zinc dithiophosphate (ZnDTPs) additive. ZnDTPs are one of the most widely used additives in lubricant due to their antioxidant and anti-wear properties via forming very thin layers on metal surfaces [4,43]. Other signals found on the APCI data at positive aKMD values include the dithiophosphates dimers at aKMD 0.434, which can be consistent with ZnDTPs, having lost their metal. Interestingly, a series attributed to a combination between a thiophosphate and a thiocarbamate was highlighted at aKMD 0.354, which could be consistent with exchange processes between molybdenum and zinc additives, as was described by Kiw et al. [44]. Two antioxidant families were also identified with ADPAs' (N1) distribution at aKMD 0.09, and they hindered phenolic antioxidants (O₃) at aKMD 0.129, including the $C_{25}H_{42}O_3$ molecule. Other signals that can be found between aKMD 0 and 0.2 were majorly attributed to base oil molecules (HC, N₁, S₁). The presence of such a distribution was expected because base oil constitutes near 80% of formulated lubricants. DBE vs. C# maps of HC and S1 compounds class obtained with APCI data were plotted in Figure S2. Base oil molecules were found between C15 and C40. The presence of such molecules is coherent with mineral base oils. The N1 compound class was not presented because base oil nitrogen-containing ions were overwhelmed in relative abundance compared to the ADPAs' ions.



Figure 3. aKMD plots obtained with (**a**): APCI(+) and (**b**): ESI(-) results for the native lubricant (NL) sample. The color scale indicates the number of oxygen atoms.

The aKMD plot obtains from the ESI(-) mass spectra in Figure 3b only displayed positive aKMD values. The families of ZnDTPs and MoDTCs were not ionized due to the absence of acid function in these molecules. The presence of dithiophosphate molecules was evidenced at aKMD 0.220. Although these compounds are well known as ZnDTPS degradation products, it seemed unlikely in this case, since these compounds were observed in the native state of the lubricant [45], and it could thus correspond to native additives as dithiophosphate can also be used to improve the durability of base oils [46]. The single point at aKMD 0.151 containing four oxygen atoms corresponds to the ion at m/z 293.17 that is described in Figure 3b. As this ion was found in NL and AL, two putative structures were proposed, with the one on the left corresponding to a probable oxidation product of the C25H42O3 molecule, whilst the other proposed structure could be consistent with a native additive because this form was described in a patent as a stabilizer for thermoplastics [47]. The major compound at aKMD 0.128, which was found at m/z 389.30, corresponded to phenolic antioxidants $C_{25}H_{42}O_3$. Other series of hindered phenolic antioxidant (O1) were characterized at aKMD 0.069. These compounds, which were only observed by ESI, corresponded to derivates of Butylated Hydroxytoluene (BHT), which is a very commonly used antioxidant [48]. These results demonstrated the interest in combining APCI and ESI

in order to have an exhaustive characterization of additive families and their polydispersity for formulated lubricants.

3.4. Characterization of Aging

Once the NL had been characterized at the molecular level, the different aged lubricants (AL) were studied using aKMD plots. In the first instance, NL and AL-3d were compared in Figure S3 for APCI results in order to have a general view of the changes of the sample compositions with aging. This allowed us to evidence a disappearance of several additive families, such as ZnDTPs, DTPs, and MoDTCs, from the first point of aging (AL-3d), and it highlighted the drastic changes in composition with aging. Indeed, a large number of compounds appeared with aging in the area between aKMD 0 and 0.4. This is why this is the area that was focused on for characterizing aging in the following discussion.

As the data obtained by APCI after aging were extremely complex, they were filtered to present, on one side, the compounds without nitrogen and, on the other side, the compounds containing at least one nitrogen atom. Figure 4 presented the aKMD plots of NL and the different AL for the compound without nitrogen. The aKMD plots were cut into four parts in order to study the behaviour of the sample with aging. The first section (1) contained mainly base oil molecules in the NL (Figure 4a Section (1)). Section (1) of the AL samples (Figure 4b–f) clearly evidenced both the occurrence and the increase in base oil oxidation products, which were mainly attributed to compounds of the CHO_{1-2} class. These compounds corresponded to primary oxidation phase products, which means aldehydes, ketones, and carboxylic acids. By increasing the aging time, a relative decrease in base oil HC molecules can be observed at the expense of the primary oxidation phase products, which increase in relative abundance. The second section (2) of Figure 4 included the hindered phenolic antioxidants (CHO₃). Contrary to several additives families that were no longer found in their native structure from 3 d of aging, these phenolic antioxidants were found in each state of aging, although their abundance seemed to be gradually decreasing. The third section (3) of Figure 4 contained no molecules in the case of the NL samples, while several products were observed for the AL samples. For instance, a series of CHO_3 molecules can be evidenced from AL-3d (Figure 4b). The occurrence of such molecules could be consistent with the peroxy radical trapping mechanisms of BHT type molecules, which is widely described in the literature (the mechanism and structures presented in Figure 4 Section (3) below the maps [39]). Few other molecules were found in this section for AL-3d and AL-5d (Figure 4b and 4c, respectively). Interestingly, an increase in the number of products was observed in this section between AL-7d (Figure 4d) and AL-9d (Figure 4f). These products were found above m/z 600 and contained three to six oxygen atoms, which could be attributed to secondary oxidation phase polymerization products (dimers and trimers). These mechanisms were described in the literature with high-temperature (>120 °C) lubricant degradation, which led to the formation of highmolecular weight oxidation products [39,49]. Surprisingly, no degradation products of ZnDTPs were detected in the AL samples, regardless of the aging time. Indeed, dithiophosphate molecules were described as the first stage decomposition products of the molecules of ZnDTPs, but none were detected even in the early state of aging (AL-3d). Jones and Coy described more advanced stages of decomposition products of ZnDTPs with the formation of trialkyltetrathiophosphates, dialkyl sulfide, alkyl mercaptans, or dialkyl disulfide [50]. The formation of low-sulfur phosphorus polymer can thus lead to the formation of oil insoluble compounds and precipitate. However, no such compounds were detected in the AL samples.



Figure 4. aKMD plots of filtered APCI data, including all species without nitrogen for: (a) NL, (b) AL-3d, (c) AL-5d, (d) AL-7d, (e) AL-8d, and (f) AL-9d. Plots were cut into four sections, and the hypothetic structure of the major products of each section were drawn under the plot.

The last section (4) of Figure 4 also displayed an empty area for the NL, while oxidation products occurred in the different AL samples. These oxidation products, containing one or two oxygen atoms, were separated by gaps of 56 Da corresponding to the C4H8 repetition unit, which is consistent with polyisobutylene (PIB) dispersant degradation products. PIB dispersants are amphiphilic additives that are used to suspend unwanted components in the oil, with the most commonly used ones corresponding to polyisobutenyl succinimide dispersants [51]. The occurrence of such degradation products was described by Gonon et al., who demonstrated that aldehydes, ketones, and β -lactones are obtained by thermo and photo-oxidation of PIB [52]. Surprisingly, no PIB dispersant was characterized in the NL (APCI or ESI), and this was probably due to the molecular size of these additives in their native form (1000–2500 Da), which makes them more difficult to ionize.

The presence of polyisobutenyl succinimide dispersant oxidation products seemed to be confirmed by looking specifically at the compounds containing nitrogen (Figure 5).

Indeed, in second section (2) of Figure 5, the occurrence of NO_x oxidation markers separated by 56 Da was also evidenced. They were attributed to N₁O₂ compounds, and the molecular formulas fitted well (DBE 4) with PIB succinimide oxidation products as Ruffell et al. [51] described them. Interestingly, these compounds decreased significantly in relative abundance between AL-3d and AL-9d, which indicates that the dispersant was almost totally degraded at the most advanced stage of aging. The first section (1) of Figure 5 displayed the oxidation of base oil nitrogen-containing compounds with an occurrence of low DBE N101–2 products, which increased in relative abundance with aging. In the third section (3) of Figure 5, the distribution of N₁O₁ and N₁O₂ compounds appeared with aging up to m/z 900. The major oxidation product in this section corresponded to $[C_{31}H_{47}NO + H]^+$ ion at m/z 450.37, as already described in Figure 1b. This was attributed to oxidation products of the major ADPAs $[C_{30}H_{47}N + H]^+$ ion that were observed in Figure 1a at m/z 422.37.



Figure 5. aKMD plots of filtered APCI data, including all species containing at least one nitrogen atom for: (**a**) NL, (**b**) AL-3d, and (**c**) AL-9d. Plots were cut into four sections, and the hypothetic structure of the major products of each section were drawn under the plot.

To obtain information about the C=O addition location, tandem mass spectrometry experiments were carried out on m/z 450 nominal mass. On this nominal mass, $[C_{31}H_{47}NO + H]^+$ ion at m/z 450.37 was predominant since the second most intense ion $[C_{30}H_{61}O_{13}C + H]^+$ only represented 5% of its intensity. Figure 6 presented the tandem mass spectra of the precursor ion for AL-3d at several acceleration voltage values. The first fragment at m/z 324.23 appeared from 5 eV of collision energy, and it corresponded to the $[C_{22}H_{29}NO + H]^+$ ion, which meant a loss of C_9H_{18} . This loss corresponded to one of the two alkyl chains of the ADPA native molecule. By increasing the collision energy, a second fragment occurred from 15 eV at m/z 198.09, and it was attributed to $[C_{13}H_{13}NO + H]^+$. It thus corresponded to the loss of both alkyl chains of the ADPA molecule ($C_{18}H_{36}$). This fragment occurred when the precursor was almost entirely fragmented, and this can be evidenced on the energy resolved mass spectra of the precursor presented in Figure S4, which shows the evolution of precursor ion relative intensity depending on the collision energy. This proved that the C=O addition did not occur on one of the two alkyl chains. Furthermore, no fragment was obtained in which nitrogen and oxygen were dissociated. It could thus be supposed that the C=O addition occurred on the amine site of the ADPA.



Figure 6. Tandem APCI mass spectra of m/z 450 nominal mass including $[C_{31}H_{47}NO + H]^+$ ion at m/z 450.37. Measurements were set at different voltages, and the hypothetic structures of the precursor and the fragments were annotated. Red arrows indicate possible fragmentation routes.

As was described for the hindered phenol peroxy radical trapping mechanisms (Figure 4, section (3)), these products could correspond to interaction products between ADPAs and radicals with the trapping function mechanisms of ADPAs at high temperature (>120 °C) [39]. Indeed, the molecular formulas attributed to these ions was in agreement with this hypothesis, since all of the structure contained at least eight DBE that were consistent with the diphenyl cores of ADPAs. In the last section (4) of Figure 5, high aromatic N_1O_x products were observed. Interestingly, the major ion at m/z 806.64 was attributed to $[C_{55}H_{83}NO_3 + H]^+$, which corresponded exactly to the addition of the major ADPA ($C_{30}H_{47}N$) with the major phenolic antioxidant ($C_{25}H_{41}O_3$), with two additional DBE (DBE 15) that can be explained by the hydrogen deficit. It could then be supposed that the radical forms of these antioxidants reacted to form an antioxidant complex. The other ion identified in this section seemed to correspond to other antioxidant complexes with an oxygen number up to five. Finally, these complexes decreased in relative abundance with aging evidence that the native additives were probably degraded in an advanced stage of aging. It has to be mentioned that no degradation products of MoDTC were detected in the AL samples. De Feo et al. described MoDTC degradation products with the formation of the amino group R2N, and the core of MoDTCs ($Mo_xS_yO_z$) are generally incorporated into black particles and precipitate [53]. Although the amino group was detected in section (1) of Figure 5, no ions were found for the expected molecular formulas, which could fit with MoDTCs degradations.

The aKMD plots obtained by ESI(-) for the NL, AL-3d, and AL-9d were presented in Figure 7. As the data obtained by ESI is less complex than that obtained by APCI, all signals have been presented on these plots without filtering the data. For the interpretation, plots were also cut into three sections. In the first section (1) of Figure 7, native BHT derived antioxidants can be observed for the native lubricant (Figure 7a). Logically, base oil molecules were not ionized in ESI(-) due to the selective ionization of acids. No BHT derived molecules were further observed after aging for AL-3d and AL-9d (Figure 7b,c). Instead, base oil oxidation products were characterized, with the major one corresponding to O₂ ions. These molecules can be attributed to carboxylic acids, which correspond to primary oxidation phase products, and they became major signals of the mass spectrum for AL-9d as it was observed in Figure 2. The second section (2) of Figure 7 contained ADPAs and hindered phenolic antioxidants O₃. It was interesting to note that almost no interaction products between antioxidants and radicals with the trapping function mechanisms of ADPA/BHT were observed in the AL samples. Indeed, these products were very high in relative abundance with APCI results. This could be in accordance with the proposed structure of the interaction products in Figures 4 and 5, with no acid functions available. As a matter of fact, peroxy radical is fixed to the amine function of ADPAs according to the trapping function mechanisms of ADPAs at high temperature (>120 °C), so the amine function can no longer be deprotonated as for the native ADPAs. It could thus be that important decreases in relative abundances occur for both antioxidant families with aging. Still, in section (2) of Figure 7, more products were observed above m/z 600 for the AL-9d sample (Figure 7c) compared to the AL-3d sample (Figure 7b), which could also be coherent with polymerisation of base oil oxidation products. In addition, polyisobutenyl succinimide dispersants oxidation products were also characterized in the second section (2) of Figure 7 for the AL samples. The attributed molecular formulas remained in accordance with what was obtained with APCI. The third section (3) of Figure 7 displayed dithiophosphate ion series for the NL as it was previously described in Figure 3. Only one ion of this series remained after aging, which also evidenced a very fast degradation of these additives with aging. Interaction products between ADPAs and phenolic antioxidant (O_3) were detected in this section for both of the AL samples. However, they remained very few and low in relative abundance compared to those observed in APCI. This could suggest that interaction occurred between the amine function of ADPAs and the hydroxyl function of the phenolic antioxidant, which would neutralize the two acid functions of these molecules. The presence of highly oxygenated base oil oxidation products (O_{5-7}) can be observed in AL-9d. These molecules were mainly found below m/z 600, which could lead us to suppose that these molecules did not correspond to polymerization products but, rather, to highly oxidized monomer.

Figure 7. aKMD plots of ESI data for: (a) NL, (b) AL-3d, and (c) AL-9d. Plots were cut into four sections, and the hypothetic structure of the major products of each section were drawn under the plot.

4. Conclusions

In this study, we demonstrated that native and aged lubricants can be characterized efficiently by high-field FTICR mass spectrometry, which allowed the elucidation of molecular composition changes with aging. The combination of positive ion mode APCI and negative ion mode ESI ionization sources allowed a wide range of chemical compounds to be covered. The use of aKMD plots with ESI and APCI data allowed a wide variety of native additive families to be characterized. MoDTCs' friction modifier, ZnDTPs' anti-wear, and ADPAs' antioxidant additives were all observed with APCI. Other additive families, such as dithiophosphate, BHT-derived antioxidants, and phenolic antioxidants (O₃) L135, were all selectively detected by ESI.

The aging of lubricants was characterized by a rapid consumption of certain additive families, such as MoDTCs and ZnDTPs, which were no longer found in their native structures from the first aging state at 3 days of aging. Studies of the mass spectra revealed the appearance of many compounds in the aged lubricants that were characterized by Gaussian distributions. aKMD plots with APCI and ESI allowed the elucidation of molecular composition changes, which can be summarized as follows:

(i) Primary oxidation phase base oil products were observed in the early stage of aging with the occurrence of aldehydes, ketones, and carboxylic acids. The secondary oxidation phase base oil products were mainly found in an advanced stage of aging (8–9 days), and they were characterized by high molecular weight molecules (>m/z 600) corresponding to polymerization products. The presence of highly oxygenated base oil monomer (O_{5–7}) were also characterized by ESI for the advanced stage of aging.

(ii) Other products were highlighted toward the high mass, but were mainly highlighted in the early stage of aging, and they were attributed to interaction products between peroxy radicals and BHT/ADPAs antioxidations due to their trapping mechanisms at high temperature (>120 $^{\circ}$ C). Antioxidants were the additives most resistant to aging, as they can still be observed at the highest aging points, although they were much less intense in relative abundance.

(iii) Antioxidants complicate products between ADPAs and phenolic antioxidant (O₃), and it was supposed in this study that this was due to the attributed molecular formulas. The major ion attributed to these antioxidant complexes corresponded to the addition of the major ADPA and phenolic antioxidant. It was supposed that these interactions occurred between the radical form of the molecules, which then linked between the amine function of ADPAs and the hydroxyl group of phenolic antioxidant molecules.

(iv) Additive degradation products were also evidenced by the formation of new products in aged samples presenting gaps of 56 Da. These products were logically attributed to PIB dispersant degradation products. The presence of such additives was confirmed by investigating the nitrogen-containing compounds (APCI) with presence of polyisobutenyl succinimide dispersant oxidation products that were also separated by 56 Da.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/lubricants11080345/s1, Figure S1: Stock solution of NL and AL samples solubilized in toluene; Figure S2: DBE vs C# maps of HC and S1 compounds class obtained by APCI for the native lubricant sample; Figure S3: aKMD plots obtained with APCI data for: (a) NL, and (b) AL-3d; Figure S4: Energy resolved mass spectra (APCI) of the ion at m/z 450.37

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