Ageing of Aircraft Lubricants

António Luís Banza de Sá

Thesis to obtain the Master of Science Degree in

Chemical Engineering

Supervisors: Prof. Carlos Manuel Faria de Barros Henriques
: Prof. Patrick da Costa

Examination Committee

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I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the *Universidade de Lisboa*.

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Abstract

The oxidation of aircraft lubricants is a crucial issue, as it is directly linked to the correct, safe and economic running of an aircraft's motor.

With this in mind, the oxidation of a synthetic aircraft engine lubricant was studied using a laboratory scale thin film plate. The consumption of the antioxidants with time was obtained, from which it was possible to extrapolate their kinetics. These parameters were compared to those obtained in an enhanced oxidation test.

Therefore, in this experimental setup, a neopolyol ester lubricant was oxidized in an open cylindrical stainless-steel container, under 180ºC, both with and without additives.

Resorting to FTIR and HPLC analysis, it was possible to observe the influence of the different additives on the oxidation process, as well as the consequences of each experimental conditions.

Keywords

Aeronautic lubricant, neopolyol ester, antioxidants, radical oxidation

Resumo

A oxidação de lubrificantes aeronáuticos é um tema de elevada importância, visto que este fenómeno está diretamente ligado com a operação correta, segura e económica do motor de uma aeronave.

Como tal, a oxidação de um lubrificante sintético aeronáutico foi estudada recorrendo a uma placa de escala laboratorial. De modo a desempenhar este estudo foram extipulados os consumos dos antioxidantes ao longo do tempo e as cinéticas destes processos. Estes parâmetros foram comparados com os resultados obtidos num teste de oxidação aumentada.

Portanto, de modo a desenvolver este estudo, um lubrificante composto por éster de neopoliol foi oxidado num recipiente laboratorial cilíndrico de aço inoxidável, a uma temperatura de 180ºC, tanto com e sem antioxidantes.

De modo a estudar a influencia dos diferentes antioxidantes e das divergentes condições operatórias no processo de oxidação do óleo, recorreu-se aos métodos analíticos FTIR e HPLC.

Palavras-Chave

Lubrificante aeronáutico, éster de neopoliol, antioxidantes, oxidação radicalar

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List of Acronyms

CMBM	Global-market based measure
CORSIA	Carbon Offsetting and Reduction Scheme for International Aviation
ICAO	International Civil Aviation Organization
SPC	Standard Performance Capability
HPC	High Performance Capability
HPLC	High Performance Liquid Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
TAN	Total Acid Number
PAN	Phenyl-1-naphtylamine
DODPA	Dioctyldiphenylamine
TCP	Tricresylphosphate
GC-MS	Gas Chromatography and Mass Spectrometry
TGA	Thermogravimetric Analyzer
DSC	Differential Scanning Calorimetry
TLC-MS	Thin-layer Chromatography and Mass Spectrometry
DAD	Diode Array Detector
THF	Tetrahydrofuran
ACN	Acrilonitrile
ATR	Attenuated Total Reflectance

List of Symbols

C	%Concentration of additive at time t=t
C_0	%Concentration of additive at time t=0
k_c	Kinetic Constant, h^{-1}
t	Time, h
Nu	Nusselt number
Ra	Rayleigh number
Pr	Prandtl number
C_p	Heat capacity, J/kg.K
μ	Dynamic viscosity, Pa.s
k	Thermal conductivity. W/m.K
Gr	Grashof number
g	Gravitational acceleration, m/s^2
β	Fluid thermal expansion coefficient, K^{-1}
T_s	Surface temperature, K
T_∞	Temperature at infinite, K
L_c	Characteristic length, m
ν	Kinematic viscosity, m^2/s
h	Heat transfer coefficient, $W/m^2.K$
ρ	Density, kg/m^3
T_f	Average temperature between T_s and $T_{\infty,}$ K

Chapter 1

Introduction

This chapter focuses mainly on providing a general perspective on the aviation industry, more specifically aircraft lubricating oil. Furthermore, the reasoning behind the development of this work, as well as its content, are listed.

1.1. Overview

Ever since the 1950's that the aviation industry has grown dramatically. This coincided with a growing interest in the development of civil aircrafts, turning air travel into a mainstream means of transport. This prosperity was due, among other factors, to the globalization of the world and was propelled by the creation of low-cost airlines, providing ever more affordable options. Nowadays, over 3.5 billion people worldwide [1] resort to air travel every year and these figures are projected to remain growing for the foreseeable future [2]. Even though, civil transportation represents the bulk of the industry, it is also comprised of military aviation, as well as air freight shipping which saw a similar rise in popularity in the past few years, due to its efficiency and overall quickness in the delivery of goods over great distances.

Additionally, there is a concerted effort by the industry to reduce its carbon footprint. Environmentally conscience programs have been developed and put in place to attempt to create an eco-friendlier aviation industry. This is especially visible in the civil aviation sector, where there is an attempt to achieve carbon neutral growth from 2020 onwards and reducing by half the carbon emission levels of 2005 by 2050, through programs like the Global-market based measure (CMBM) [3] and the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA) [3] of the International Civil Aviation Organization (ICAO). Furthermore, in a more general scope, environmental policies such as the European Community's REACH legislation and worldwide equivalents, influence the additive packages employed both in the airplanes fuels, as well as in the lubricating oils used in the aircrafts engines, promoting safer and more ecological blends [4].

Therefore, given this panorama, aircraft manufacturers are under greater and greater scrutiny to develop better, more powerful, more efficient, more ecological and economical aircrafts. To comply with these demands, there have been constant efforts in multiple fronts, be it the development of more ecological and sustainable aviation fuels, as well as in the improvement of fuel efficiency, for example by using lighter and stronger composite materials, which allow for higher combustion temperatures, more efficient working of the engines and a better overall power assignment due to the fact that the aircraft is lighter, when compared to the alternatives, such as metal alloys and ceramics [3]. Another point of focus is on the lubricating oil systems.

Lubricating oils are essential for the correct running of an aircraft's jet engine. First of all, they are obviously responsible for the lubrication of the multiple components of the gear boxes, meaning they are responsible for reducing the friction of moving parts and reduce wear derived from the direct contact of different components. Additionally, the lubricant is also responsible for dispersing heat away from the gears, in conjunction with the removal of dirt and any kind of debris from the engine, as these may cause issues in the engines operation [5].

Both in economic and environmental terms, nowadays, the lubricating oil systems have a huge issue, as there is a loss of oil during flight, mostly in the demisters. This leads to the need for an oil top-up every time the aeroplane lands. However, this top-up is beneficial to the plain's operation, as the mixture of new and used oil is enough to replenish the oil’s additives and counteract its degradation, avoiding the need for the complete substitution of the oil.

Anyway, as aircraft engines evolve, they tend to reduce the amount of oil loss during flight and hence reduce the regularity and quantity of top-ups, progressively reducing the replenishment of additives. Furthermore, the conditions to which the oil is exposed to are progressively harsher as well, as motors become more powerful and work at higher temperatures, leading to a faster degradation of the oil and its properties. Since, the periodic drainage of the oil system is not an economically viable option, lubricating oils need to become ever more resistant to degradation. Therefore, to develop more resistant and efficient oils and oil systems, it is essential to fully understand how the lubricating oils degrade with time [6]–[8].

One of the greatest factors contributing to the degradation of these oils is the process of radical oxidation [9]. This occurs when the oil is submitted to high temperatures while in contact with oxygen. Under these conditions, the oil undergoes some chemical and physical changes. These changes have some obvious and clearly visible consequences, being a change in the oil’s color or the formation of sludge and deposits; as well as some less visible changes, namely the degradation of the chemical integrity of the base oil’s structure and some of its other constituents. Most of these changes are detrimental to the correct operation of the aircraft. Hence, antioxidant additives are employed to counteract this degradation.

Oil manufacturers retail two different types of oil, the Standard Performance Capability (SPC) and the High Performance Capability (HPC). These differ in the antioxidants used, the former use secondary amines, while the latter use oligomers of unknown formulation. However, only the SPC oil was studied under the scope of this thesis, as it is the most commonly employed oil type in an aeronautical context, as well as the most characterizable oil.

Using laboratory scale apparatus oil samples were degraded and analyzed using both high performance liquid chromatography (HPLC) and Fourier transform infrared spectroscopy (FTIR).

1.2. Motivation and Contents

Unlike the degradation of automotive lubricating oils, thus far, the degradation of aircraft engines is still a reasonably untapped topic. However, as previously stated, given the scrutiny of the industry, it is vital to fully comprehend the mechanisms involved in the degradation of such oils, since, this knowledge would ultimately translate to a safer, more ecological, more efficient and more economical running of aircraft motors.

As such, in a joint venture between Sorbonne University and Safran Aircraft Engines, this internship was focused on the study of the degradation of aircraft lubricating oil.

These findings will be displayed in this 5-chapter thesis. After the introduction, an exposé on the theoretical background and state of the art will be done. This will be followed by the description of the analytics processes of the experimental part. The experimental data and its interpretation will ensue. As for the final chapter, the main conclusions of the whole thesis will be stated, summarizing the main results and developments of this 6 months project.

Chapter 2

Theoretical Background

In this chapter some simple questions about lubricating oils will be answered, such as what their purpose is, what they are made of and how they function. As such, the chapter provides some basic concepts and general information on aircraft aviation oils, as well as a more in-depth look into the radical oxidation mechanism. The state-of-the-art is also presented.

2.1. General information

First of all, lubricating oils, have the very obvious purpose of lubricating some parts of the engine’s mechanical parts. They do so by being sprayed on gears and bearings and forming a thin film between these moving parts, this film prevents the direct contact between the mechanical parts, reducing friction and mechanical abrasion, therefore allowing for the proper, more effortless and efficient running of the motor, as well as increasing the longevity of the mechanical parts [5].

Additionally, the oil is also responsible for the dissipation of heat from these regions, so that they do not overheat, hence avoiding the development of weak spots and issues in the materials structure [5]. Furthermore, it is also accountable for cleaning the regions it flows through, by carrying impurities, such as dust, material debris, varnishes and gum, to filters, so that these contaminants are removed from the engine’s system, avoiding the engine’s clogging or breakdown [5]. Both these functions are becoming progressively more important, as engines develop and work under harsher conditions, with smaller tolerances for mistakes.

2.1.1. Main oil properties

Therefore, in order to be able to comply with these demands, oil manufacturers must have some specific properties in mind. Some of the most commonly registered properties in oil specification sheets are viscosity, pour point, flash point, fire point, total acid number and water content [10]–[12].

Viscosity is a very important property for assuring the correct lubrication of the system, as it needs to be, at operating temperatures, low enough that the oil can flow freely between adjacent fast-moving parts, however it should also be high enough for it to have a proper retention time on these parts, providing the desired wear reduction effect [13].

The pour point is the temperature at which a liquid is no longer able to flow. Therefore, this is an important characteristic for the proper running and maintenance of the engine, as it should be low enough for the oil to flow in the system in cold starts at low temperatures, as well as for an operator to be able to replenish the oil reservoir at any atmospheric temperature [13].

Other important properties are the flash and fire points, these are the temperature at which the oil would start to burn or vaporize, respectively. These should be high so that these events do not occur during flight, as they would lead to a malfunction of the engine, hence putting at risk the safety of any person aboard the aircraft [13].

The total acid number, or TAN, provides information on how acid an oil is. It is a measurement of how much base, potassium hydroxide, is necessary to neutralise an oil, so it is expressed in mg of potassium hydroxide per g of sample [13]. This is a crucial characteristic when studying the degradation of the lubricating oils, as during their degradation process, acids are formed, therefore, naturally, the TAN increases; hence by comparing the TAN at that point and the initial TAN, one obtains an idea of how degraded an oil is.

The water content, refers to the amount of water that is present in the oil, which can be found dissolved in the oil, as a free liquid or as an emulsion [14]. Aeronautic oils should have a minimal water content, as close to zero as possible, as water can cause operational issues, as at low temperatures it can solidify into ice. Additionally, water can also potentially promote the corrosion of metallic parts of the lubricating system and may lead to the undesired enhancement of the catalytic decomposition of the base-stock [15].

Therefore, to maintain the high standards necessary, both in terms of the engine's operation, as well as in terms of safety concerns, oil manufacturers must produce oils that have these characteristics, and some others, within specific industry parameters. In an attempt to produce a robust oil, with high thermal and pressure resistance, that assures a correct, efficient and safe running of the engine.

2.1.2. Oil composition

According to the American Petroleum Institute, lubricating oil's base stocks can be categorized into five different groups, Groups I to V [4].

Base stocks belonging to Group I are the least refined, they are petroleum derived paraffinic mineral oil, normally extracted through fractional distillation, hence containing some potentially pollutant sulphur, oxygen and nitrogen compounds [4].

Group II base stocks differ from the Group I oil due to the fact that they are hydrorefined, making them more refined oils and more receptive to additives, with a lower sulphur content, as well as a lower amount of polar constituents [4].

Group III are even more refined petroleum-based oils, they are submitted to hydrocracking processes. This creates a more constant and uniform oil composition and viscosity, making it overall much more stable [4].

Group IV refers to synthetic polyalphaolefinic oils, these are no longer petroleum derived, as they are chemically synthesised. These are also very stable, as they have a definable uniform composition, with little to no impurities, conferring great properties to this kind of base-stock. However, these may have some material compatibility issues [4].

As for Group V, all the remaining possible oil base-stocks, not catalogued in Groups I through IV, are covered by this category. The great majority of these base stocks are synthetic ester and polyester oils. These tend to be the premium oils, with the more favourable overall properties [4].

Out of all these options, in the aviation industry, synthetic group V oils are the preferred choice to employ, as the lubricating oil's base stock, as with these it is possible to develop quite a robust and well-rounded oil, which is able to withstand the very harsh conditions to which the lubricating oil is submitted to in the jet engine. The favoured esters of this group are the neopolyol esters, shown in Figure 1.

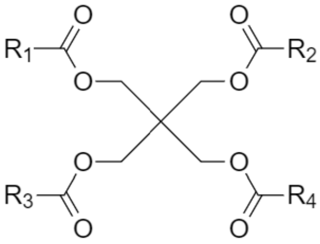


Figure 1 - Structure of a neopolyol ester.

The most significant characteristic of these specific esters is their exceptionally high thermal stability, which is especially interesting moving forward, as engines develop and work at higher temperatures. This is due to the fact that, neopolyol esters do not have a hydrogen in the β position relative to the single bonded oxygen in their structure, as these esters are made to have quaternary carbons in this location [6], [16]–[18]. This is significant, as the presence of these hydrogens leads to the thermal degradation of esters at high temperatures, through a mechanism known as β-elimination, shown in the chemical reaction of Figure 2. Therefore, since these esters lack hydrogens in this particular position, this type of attack does not occur, automatically making them very thermally stable, when compared to other esters.

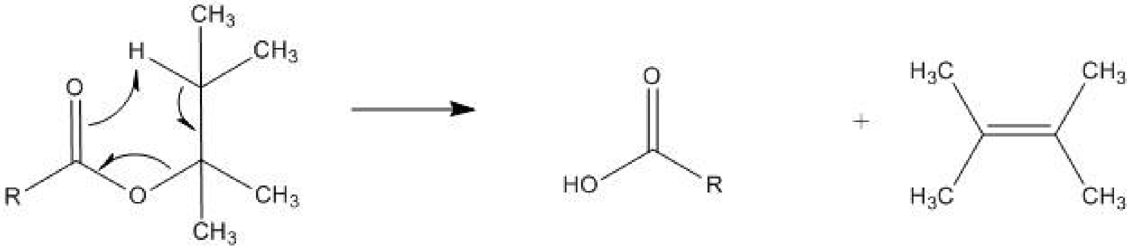


Figure 2 - β-elimination [16].

Additionally, they also show some general inherent advantages from being an ester, such as having low volatility, meaning a high flash point, and inherent anti-wear and detergency properties, which stem from the intrinsic polarity of the ester's structure [16]. This polarity allows for favourable interactions between the ester molecules and the metal structures, which translate into anti-wear abilities, and contrasts with the non-polar hydrocarbon chains of the esters structure, making it an amphiphilic molecule, providing its dispersant properties, which translate into a reduction in deposit and varnish formation, as well as a greater ability to dissolve additives [16], [18].

Another advantageous feature of the neopolyol ester, as a base stock, is its intricate molecular structure, as represented in Figure 1. This provides some protection towards oxidative attacks and the onset of radical oxidation, which is one of the greatest contributors to the oil's degradation, this process will be described in greater detail later on. The complex structure of the neopolyol molecule provides steric hinderance to hydrogens susceptible to dissociating when in contact with oxygen, shielding and protecting them, to a certain degree, from the occurrence of these oxygen attacks [16].

Furthermore, when compared to petroleum based base stocks, synthetic esters are eco-friendlier and present a better sustainability, as they are less likely to contain impurities or undesired compounds in its composition, as they are produced from pure reactants. Furthermore, these reactants may be biomass derived and overall, synthetic esters present a greater biodegradability than petroleum-based products [16], [18].

2.1.3. Additives

Even though the oil's base stock is very important and grants the overall oil a great part of its properties, commercial oils also contain an additive package. These additive packages can account up to around 20% of the volume of the lubricant [4] and differ from manufacturer to manufacturer as well as in each different product. They contain a great variety of chemical compounds, each with the purpose of enhancing or developing specific characteristics the base oil lacks.

As previously stated, one of the most important additives present in these packages are those that prevent the oxidative degradation of the ester-base oil, which are the antioxidants. These can either work by trapping free radicals, by donating a hydrogen atom; or by decomposing peroxides, they are known as primary and secondary antioxidants, respectively [5]. There is an additional, less noteworthy, class of antioxidants, known as metal deactivators, which bond with metal ions reducing their catalytic activity [5], [19]. Therefore, antioxidants mostly work by preventing the onset of the initiation and propagation reactions of the degradation.

The main antioxidants used in the aeronautic industry are phenyl-1-naphtylamine (PAN, $C_{16}H_{13}N$) and dioctyldiphenylamine (DODPA, $C_{28}H_{43}N$), which are both secondary amines, as seen in Figure 3. As antioxidants, they work by donating, preferentially, the hydrogen from their N-H bond to radical species, preventing the propagation of the radical reaction, hence, both are primary antioxidants. This N-H bond is particularly susceptible to attacks from peroxy radicals, due to its low dissociation energy [20], as seen in Table 1. However, due to the valency of the nitrogen atom and intricate ring structure of these molecules, they are able to harbour a free electron, while remaining a stable molecule, which no longer propagates the radical reactions.

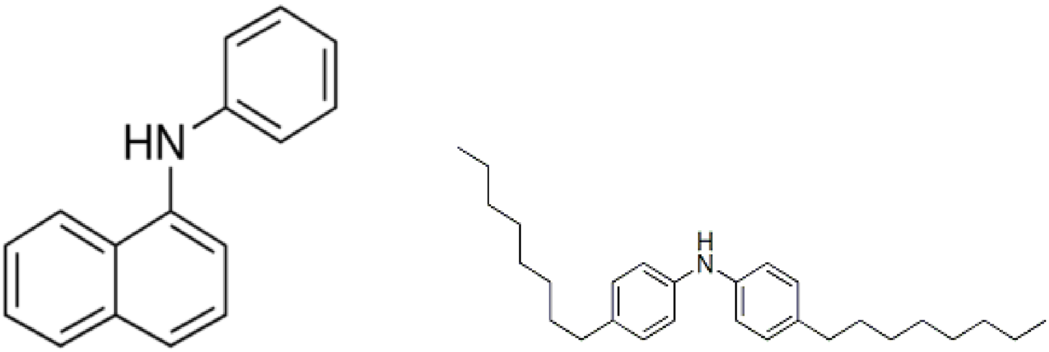


Figure 3 - Chemical structure of PAN (Left) and DODPA (Right).

This kind of antioxidant is preferred due to its ability to regenerate after it has reacted with the radicals, furthermore the products from their reaction also have antioxidative activity. Therefore, given all this, secondary amines have the ability to consume a great number of radicals, making them more effective than the alternatives, such as hindered phenols [21], [22]. Furthermore, they are also safer compounds, than the alternative sulphur or phosphorus antioxidants, which may produce harmful oxides, corrosive by-products and promote polymerization, leading to potential sludge formation [21].

Other than the antioxidants, another very important class of additives is the anti-wear agents. This type of additive has progressively become significantly more important, as engines become more powerful and bearings move at greater speeds, greater wear down of these parts occurs. Therefore, these compounds are designed to create a protective cover on the surfaces the oil flows through, reducing the abrasive nature of the mechanical contact between moving parts. Nowadays, the most commonly used anti-wear, in aviation oils, is the tricresylphosphate (TCP), which produces iron phosphate compounds at high temperatures which coat the metal surfaces of the engine it encounters and reduces friction, hence working as a friction modifier [4]. TCP has also been linked to having antioxidative characteristics and synergistic effects with antioxidant additives [23].

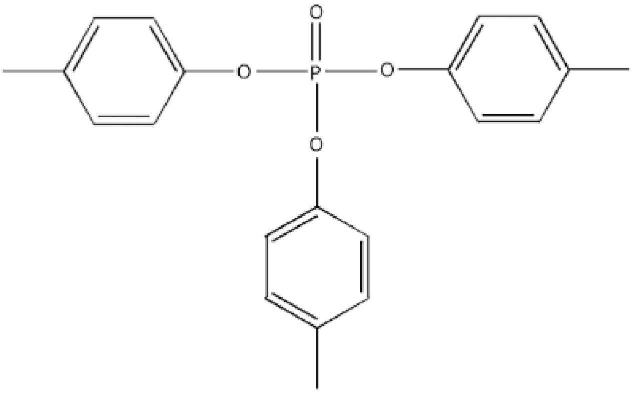


Figure 4 - TCP's chemical structure.

The previously mentioned additives are known to be contained in the employed additive packages of the commercial oils used in the experimental portions of this thesis, however, other possible additives include, rust and corrosion inhibitors, detergents and dispersants, friction modifiers, viscosity modifiers and anti-foam agents.

Rust and corrosion inhibitors are polar molecules that, like the anti-wear agents, form a protective layer on the metal's surface. This layer prevents the coated surface from getting into contact with water or acids, which are produced during the oil's degradation processes [4], [5]. It is crucial to avoid the corrosion of the motor's constituents, in order to keep the engine's structural and operational integrity.

Detergents and dispersants are also polar molecules which prevent the formation of deposits, varnishes and gums. They minimize the agglomeration of debris and impurities and suspend them in the oil's surface [4], [5]. By doing so, the oil's viscosity is maintained, the clogging of parts is avoided, and the engine is kept running smoothly.

Friction modifiers reduce friction between moving parts, reducing the undesirable production of heat, that could lead to greater wear and mechanical issues. Additionally, it also improves the overall efficiency and fuel economy of the engine, as it makes mechanical movement between cogs and bearings more effortless. Once again, these work by coating the surface of the mechanical parts [4], [5].

Viscosity modifiers are employed to attenuate the oil's viscosity discrepancy with temperature. In other words, it makes the oil's viscosity more constant for a wider temperature range. These are normally polymers which can either coil or straighten out according to the oil's temperature. At low temperatures, the molecule is coiled up, having a limited effect on the oil's viscosity. However, as temperatures rise, these tend to straighten and bulk up and interacting with the oil, increasing its viscosity [4], [5].

Anti-foam agents are employed to avoid the creation of foam, which could cause serious issues in the engine's running, as it could cause cavitation damage, limited circulation of oil, which in turn causes a potential lack of lubrication, as well as a lack of heat dissipation, as gases dissipate less heat than fluids. The creation of foam is due to an intensive mixture of air or a gas with oil, forming bubbles. Therefore, these agents act by influencing these bubbles' surface tension, making them burst, hence releasing the trapped gases [4], [5].

2.1.4. Radical oxidation

As previously stated, radical oxidation is one of the greatest factors contributing to the degradation of the lubricating oil. This fourfold reaction process occurs, at a considerable rate, when the oil is submitted to an oxygenated environment, under high temperatures, these must be at least above around 100ºC [21]. When the oil is exposed to these specific conditions the process of radical initiation begins. This is followed by the propagation, autocatalysis and termination stages [19].

The initiation step is characterized by the breakdown of the ester molecule, forming radicals, due to the extraction of a hydrogen atom from the ester's structure by an oxygen molecule [21]. The susceptibility of these hydrogen atoms to attacks is dictated by their bond's dissociation energy, which is shown in Table 1, the smaller the bond dissociation energy, the greater the probability of being attacked [21]. Additionally, radicals can also be formed due to the decomposition of hydroperoxide molecules, when in the presence of metal catalysts, such as iron or copper [21]. This initiation mechanism progressively becomes more predominant as the radical oxidation progresses and the amount of hydroperoxide compounds increases [21], as these are produced as a consequence of the subsequent steps.

Table 1 - Bond dissociation energy for each bond type, in kcal/mol [20], [21].

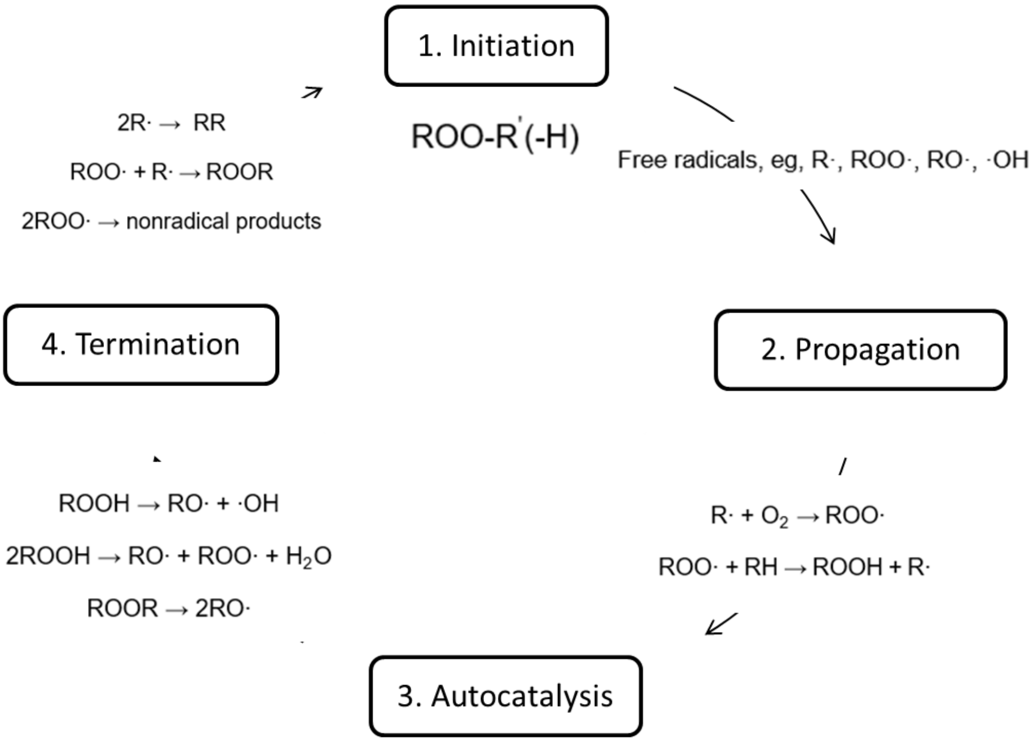
Type of bond	Bond dissociation energy (kcal/mol)
N-H	84.7 [20]
Benzylic	85 [21]
Allylic	89 [21]
Tertiary	92 [21]
Secondary	95 [21]
Primary	98 [21]
Phenyl	112 [21]

Once the radicals are formed, the propagation step immediately kicks into effect. At the early stages of the propagation step, the newly formed ester radicals react with oxygen forming peroxide radicals, which in turn further react with other ester molecules producing the aforementioned hydroperoxides [21]. Parallelly, the autocatalysis stage occurs, where the hydroperoxide compounds autonomously decompose, forming new radicals, which in turn react with ester molecules producing new radicals and some by-products [21]. Therefore, the propagation and autocatalysis steps are characterized by the further creation of radicals, where existing radicals react with original ester molecules, oxygen molecules or by-products of other simultaneously occurring reactions, forming new radicals.

The final step is the termination step. Here, radicals react with each other forming new, non-radical, stable chemical compounds [19], [21].

All of these steps are intertwined and occur simultaneously. From this whole process, a wide range of molecules are formed, such as alcohols, aldehydes, ketones, carboxylic acids, water and other esters. At an initial stage of the whole process low molecular weight products are produced and the whole fluid suffers some physical changes, such as, a lower viscous [19]. However, with time, heavier molecules are naturally formed from the radical process and with the increased concentration of some of these by-products, side reactions occur as well, ultimately leading to the formation of polymers, which can then translate into sludge and deposit formation. Overall, the oil, once again, tends to suffer some physical alterations, such as, visible colour changes and an increase in its viscosity [19], [24], [25].

Scheme 1 summarizes the process of radical oxidation described above.



Scheme 1 – Schematic representation of the 4 stages of radical oxidation and some of their mechanisms [19].

Even though neopolyol esters do have some antioxidative features and other inherent advantages, as previously exposed, these are not enough to counteract the process of radical oxidation. Therefore, as previously mentioned, the elected antioxidants for the task of inhibiting the radical oxidation process are PAN and DODPA. They both work by preventing the onset of the propagation step, by donating a hydrogen atom to free radicals they encounter. Their very complex mechanisms can be seen in Figure 5 and Figure 6, respectively.

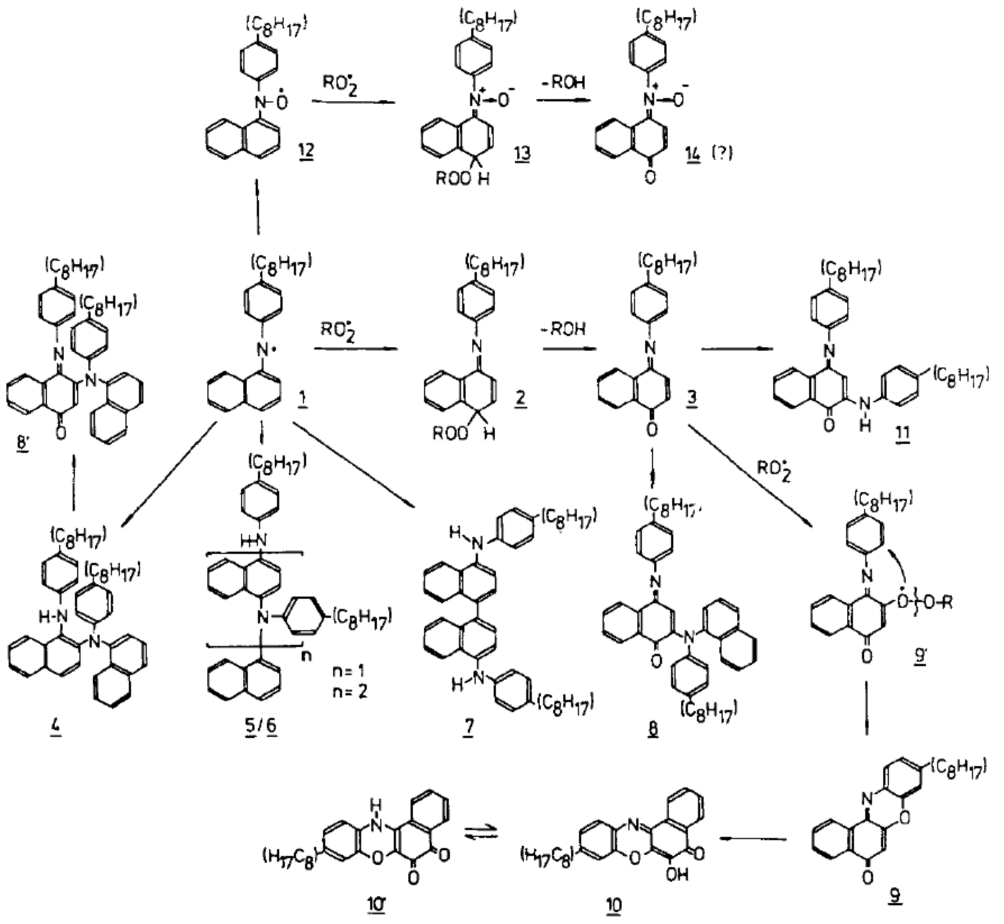


Figure 5 – Oxidation prevention mechanism of PAN [9].

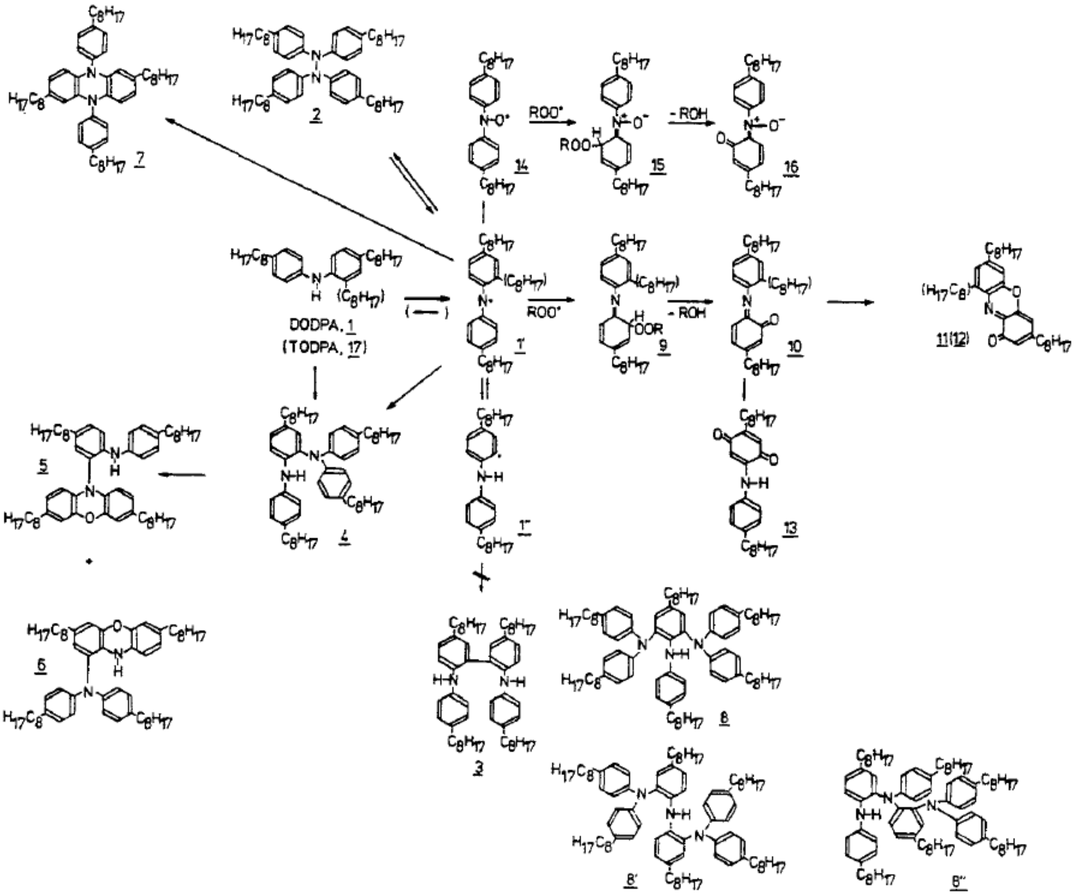


Figure 6 - Oxidation prevention mechanisms of DODPA [26].

Bottom line, out of these very complex mechanisms, it is possible to understand that both antioxidants work by donating either the hydrogen attached to their nitrogen atom or a hydrogen from one of their benzenic structures. These are preferential sites of attack, due to their exceptionally low dissociation energy, as seen in Table 1. This feature is the reason why the antioxidants are attacked preferentially and, hence, protect the ester molecules from radical attacks, as these normally contain tertiary, secondary or primary hydrogens in their possible attack sites [16], which are comparatively less likely, energetically, to react.

Unlike the radicals with which the antioxidant molecules react with, the radical antioxidant molecules do not further react, as they are quite stable due to resonance, as a result of both the benzenic structures as well as the nitrogen's valency [9]. These antioxidant radicals, tend to react quickly with other radicals [22], creating stable molecules, which can vary widely, as seen in Figure 5 and Figure 6 depending on the molecules structure and the conditions to which it is submitted to. Generally speaking, these products can be a polymer of the antioxidant, some kind of mixture of available free radicals and the antioxidant and, in some cases, there can even be a regeneration of the antioxidant molecule [9]. It is important to note that some of the potential products can exhibit antioxidant properties themselves, as they are still able to donate a hydrogen and retain a free radical in a stable fashion, this can be seen in both PAN's and DODPA's cases [9], [26].

It is also relevant to mention that synergistic effects have been observed between PAN and DODPA [22], when these are applied together, as an antioxidant additive package. When these are employed together, it has been found that DODPA is regenerated at the cost of a PAN molecule, which then proceeds in its usual mechanism, as shown in Figure 7. Employing both additives simultaneously prolongs the longevity of DODPA and, consequently, the base stock's longevity as well.

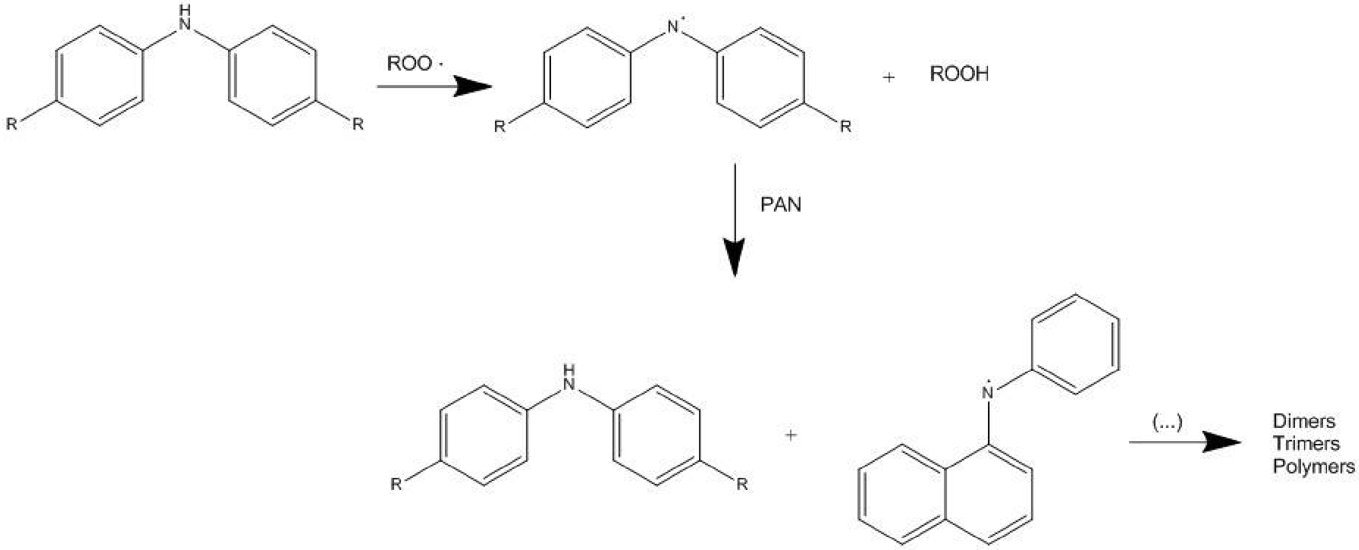


Figure 7 - Synergistic mechanism between PAN and DODPA. PAN is "sacrificed" to regenerate DODPA. In turn, PAN proceeds in its usual mechanism forming dimers, trimers and, eventually, polymers [22].

2.2. State of the art

Generally speaking, the research done in this field focusses on one of 4 different scopes, the development of better ester bases, the development of better antioxidant packages, the oxidation mechanisms and their kinetics or the employment of new analysis methods.

In terms of the development of an overall better-rounded lubricating oil, the greatest trend, in this sector, is the study of the synergistic and antagonistic effects of additives amongst themselves, meaning, how multiple additives interact and if those interactions promote antioxidative behaviour, to create better, more effective additive packages. As previously mentioned, synergistic effects have been found not only between secondary amines, like PAN and DODPA [22], as well as between antioxidants and other additives, such as TCP [23]. As for the interaction between amine and phenolic antioxidants, the later tend to cancel some of the antioxidant abilities of the former, however they still show beneficial effects, in the reduction of sludge formation, by increasing the solubility of the mixture [22].

Other than this, examples can be found on the development of more effective antioxidants [20], [27], which would react more readily with the radicals, while still being stable molecules [20]; as well as, more environmentally concisely driven research, with the development of more eco-friendly blends [18], [28].

In terms of the study of the oxidation mechanisms, nowadays, most of the research is focused towards the incorporation of new analysis tools. Common analysis methods include FTIR [24], gas chromatography–mass spectrometry (GC–MS) [24], [29], conventional thermogravimetric analyzer (TGA) [29], [30], differential scanning calorimeter (DSC) [29], among others; while some promising new techniques include isotope marking [6]; which allows for a better understanding on where the ester molecules are attacked and how the consequent products are formed; fluorescent chromatography [25] and the incorporation of some other chromatography method with the mass spectroscopy, such as thin-layer chromatography and mass spectroscopy (TLC+MS) [31]. The objective of studying these new techniques is twofold, they can provide the necessary information to understand how the degradation of the oil occurs and help confirm previous findings, as well as the development of techniques with the potential of eventually being employed in a real-life scenario, which would aid the determination of if an oil in an aircraft is still fit to keep the engine running smoothly; for example, if it contains enough antioxidants to counteract the oxidation mechanisms.

There is also an effort in the development of kinetic models to translate this complex degradation process, both in terms of the ester and the antioxidant consumption [15], [25], [30]. Through these models, predictive estimation of the antioxidant consumption and oil lifetime can, potentially, be done.

It is important to emphasize that almost all of the reviewed papers used some kind of oxidation accelerating mechanism to do their studies, through induced air or oxygen flow. The novelty of the study presented in this thesis is the use of non-enhanced methods of simulating the ageing of the oil.

Chapter 3

Experimental Procedure

In this section, the oil used, and its preparation, is describes, alongside the analysis methods.

3.1. Lubricating oil and antioxidants

The commercial lubricant used in this work is a Standard Performance Capability (SPC) oil, with neopolyol esters as its base oil. Two different antioxidants, PAN and DODPA were supplied by the manufacturer. This commercial lubricant is compared to model mixture solutions. These solutions, containing the same neopolyol ester base oil and different additives, were stirred together at 80 °C in a beaker until homogeneously mixed. The additives were added in the same proportions as those found in the commercial oil.

3.2. High Performance Liquid Chromatography

The High Performance Liquid Chromatography (HPLC) was performed on a Waters e2695 equipped with a DAD (Diode Array Detector) UV e2998. A 100 mg oil sample was first diluted in 10 mL of tetrahydrofuran (THF). A 10 µL volume of this solution was then injected into a stainless-steel column (Waters XSelect type CSH C18, 250×4.6 mm ID, 5 µm particle size). Water and acetonitrile (ACN) were used as the solvent for the mobile phase in a gradient mode. The temperature of the column was maintained at 40 °C and the samples at 4°C. The pump flow rate was set to 1 mL/min. The wavelength of detection was 254 nm. This technique was used to monitor the quantitative results of antioxidant depletion by a comparison of peak area, by taking the relative area of the antioxidant's peaks, it is possible to determine their consumption versus time on stream. It also allows to identify the appearance of any new compound.

Figure 8 shows a typical chromatograph of the lubricant before ageing. One peak at a specific retention time corresponds to one specific molecule. In this case, phenyl-1-naphtylamine (PAN) is detected at 15.75 min, while dioctyldiphenylamine (DODPA) is detected at 23.24 min.

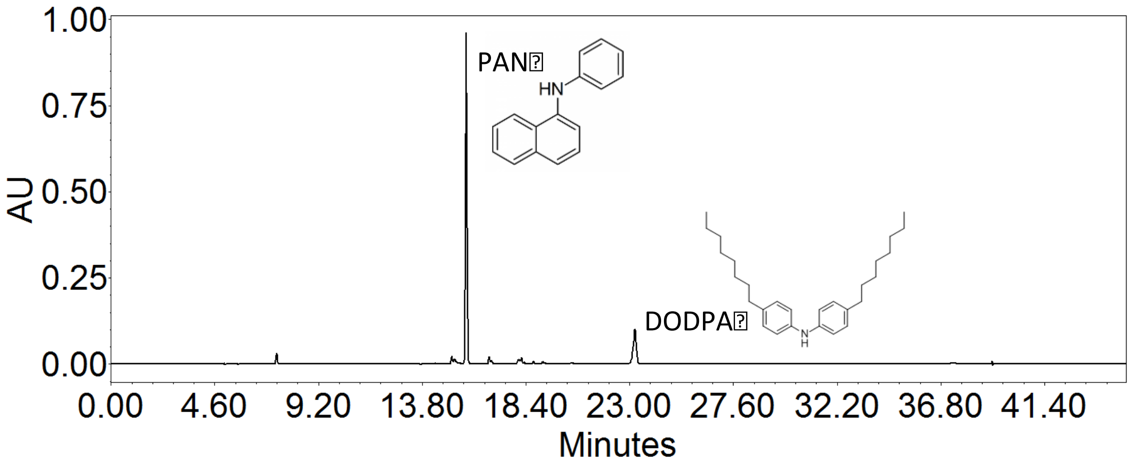


Figure 8 - HPLC chromatogram of fresh oil. Retention time of the additives: phenyl-1-naphtylamine (PAN) **15.75 min**; (middle); (right) dioctyldiphenylamine (DODPA) **23.24 min.**

3.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Bruker spectrometer TENSOR 27. A drop of lubricant was applied on an Attenuated Total Reflectance (ATR) cell equipped with a ZnSe single crystal. The spectra were recorded over the wavelength range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} using 16 scans. The FTIR was used to monitor changes to the structure of the base oil, meaning the neopolyol ester.

The main chemical bonds of the ester, i.e. the carbonyl bond C=O, appears at 1710 cm^{-1} and C-O bond is detected at 1200 cm^{-1} [32], [33], whereas C-H bonds, i.e. C-H$_2$ and C-H$_3$ can be observed at about 3000 cm^{-1} respectively [32], [33]. The analysis of the FTIR spectra, therefore, allows for the detection of ester base stock's degradation, through the simple comparison of the spectra of both oxidized oil and fresh oil. Moreover, after oxidation, the production of primary alcohols should be observed at 1050 cm^{-1} (C-O bond) and 1350-1260 cm^{-1} (O-H bond), aldehydes at 2880-2650 cm^{-1} (C-H bond) and 1740-1720 cm^{-1} (C=O bond) and carboxylic acids or also alcohols with a wide band at 3500 cm^{-1} (O-H bond) [32], [33]. This can be observed in Figure 9.

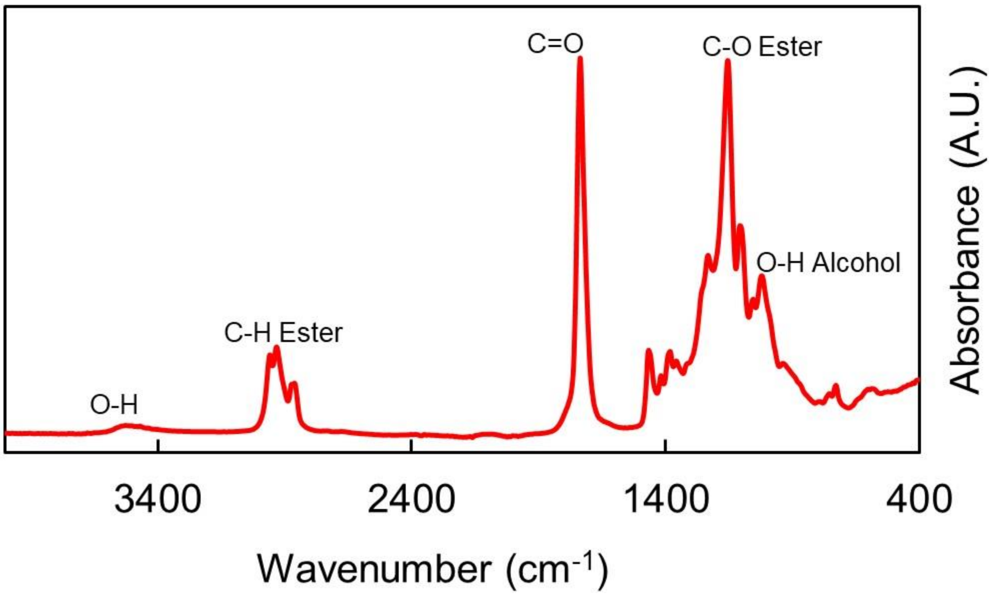


Figure 9 - FTIR of oxidized oil. Chemical bonds focused and their respective wave numbers: acid O-H bond at 3500 cm-1, ester C-H bonds at around 3000 cm-1, ester C=O bond at 1710 cm-1, ester C-O bond at 1200 cm-1 and alcohol O-H bond at 1050 cm-1.

Chapter 4

Experimental Ageing of Lubricating Oil Using a Laboratory Thin-Film Plate

The ageing of a neopolyol ester base oil is studied in this chapter. This was done using a heated open stainless-steel cylindrical container. There is a focus on the influence of the antioxidants and their role in preventing the oils degradation. A comparison, between the results obtained in this experimental setup and the results of a previously conducted accelerated oxidation test, is done as well.

4.1. Experimental Setup

The oxidation test was conducted on an open stainless-steel cylindrical container, Figure 10. In each experiment, a sample of 65mL of oil was placed on the vessel, which translated to an oil thickness of 6mm. To mimic the conditions to which the oil is submitted to in an aircraft engine, the oil was heated, using a heating plate, to a temperature of 180ºC. The experiments were conducted for 440 hours and samples were taken at times 0, 70, 130, 180, 240, 350 and 440h. However, for the FTIR plots, the only results shown are those for times 0, 70, 240 and 440h, as they are representative of the trends observed in the remaining results.

It is important to note that all the samples, in this chapter, were obtained and, the corresponding FTIR and HPLC analysis, were done by Sandrine Duong, who was conducting a PhD on the topic.

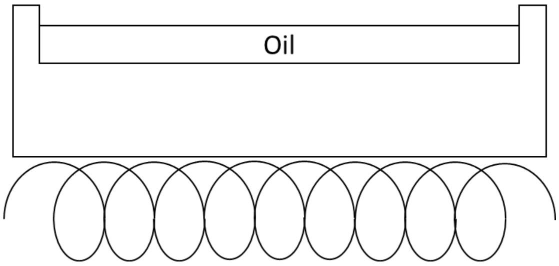


Figure 10 - Schematic representation of the oxidation test.

4.2. Results and discussion

4.2.1. Thermo-oxidative degradation of a commercial oil

By analysing the FTIR results, shown in Figure 11, it is clearly visible that the neopolyol ester in the commercial oil did not suffer any degradation, in the experiment’s time frame, as there is no clear fluctuation of the relevant peaks of the FTIR.

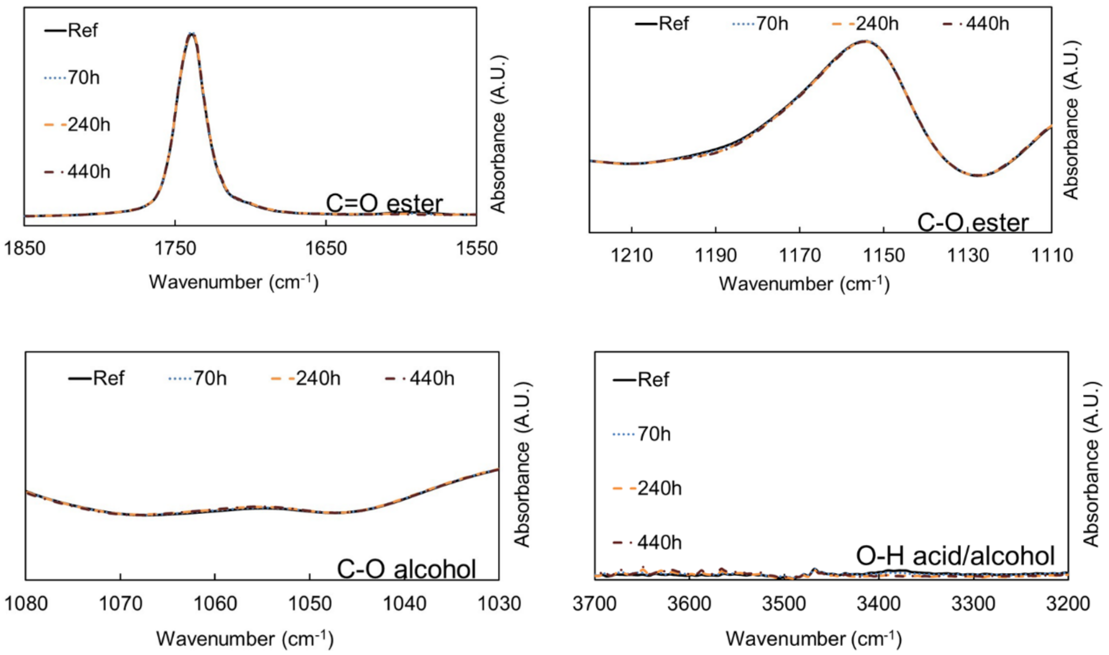


Figure 11 - FTIR analysis for the commercial oil.

As for the antioxidants present in the oil, their consumption can be analysed in the HPLC results, shown in Figure 13. From these, it was possible to extrapolate the % consumption of the antioxidant additives over time, shown in Figure 12. This plot reveals that PAN is almost completely consumed after 70h, as there is only 4% of it remaining. As for DODPA, it takes around 180h for half of it to be consumed and by the end of the experiment 27% of it was still present in the oil sample. This translates to a 86% overall consumption of the total antioxidant package.

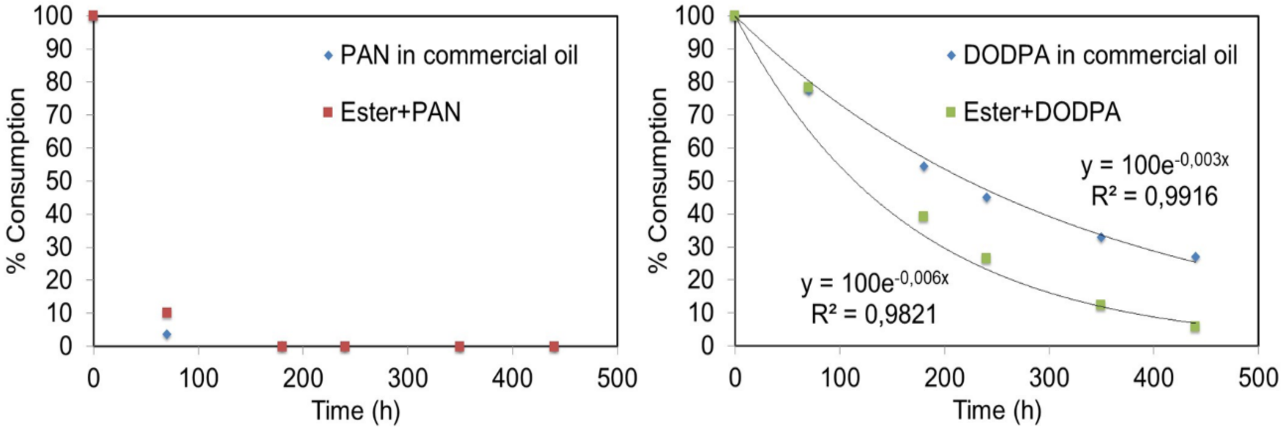


Figure 12 - The consumption of both PAN and DODPA as a function of time, both in the commercial oil and as solo additives in the ester base stock.

Assuming DODPA follows a first order kinetic model, it is possible to extrapolate, from the graph, an expression that dictates the concentration of DODPA with time and obtain the kinetic constant, k_c. For the commercial oil:

$$C = C_0 \times e^{-k_c t} \quad (1)$$

$$C = 100 \times e^{-0.003t} \quad (2)$$

From the HPLC, it was also possible to detect 19 different products, 5 of which appeared and disappeared, meaning that they were consumed over time, as is visible in Table 2. These particular products were considered to be intermediate by-products. Most likely, they were PAN or DODPA derived, as both antioxidants are known to polymerize when preventing the oxidative consumption of the oil's esters, forming active polymers which work as antioxidants as well, hence explaining why these products were consumed with time and were not detected on the HPLC [22], [34]. This assumption is corroborated by the fact that the slope of the consumption of DODPA with time changes slightly, the DODPA is being consumed at a slower rate, when the intermediates begin to be depleted.

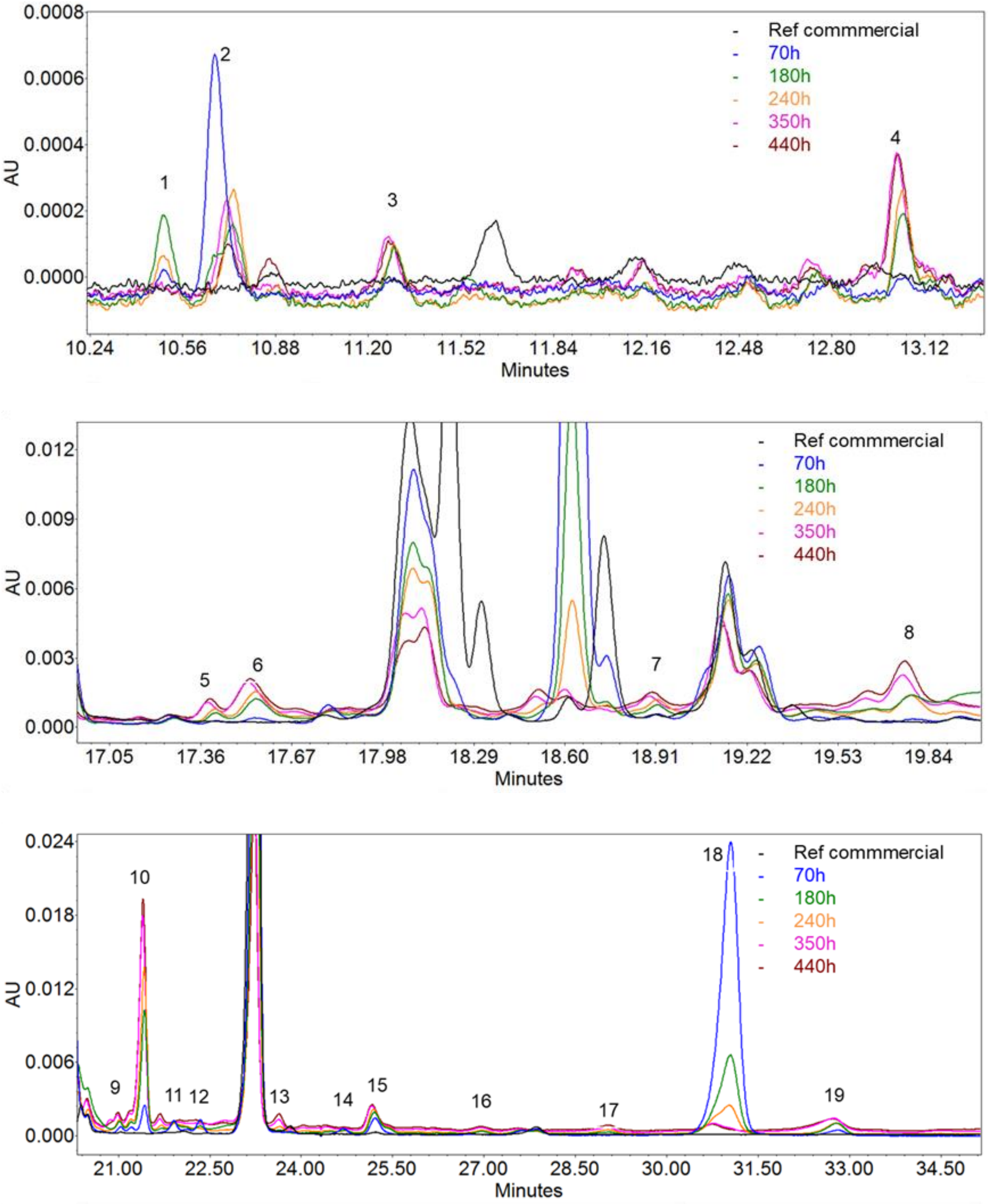


Figure 13 - HPLC chromatograms for the commercial oil.

Table 2 - Overall fluctuation of the HPLC peaks for the different products of the commercial oil.

Peak n°	Retention time (min)	70 h	180 h	240 h	350 h	440 h	Type of product	
							Intermediate	Final Product
1	10,49	+	+	+	-	-	✓	
2	10,68	+	-	+	-	-	✓	
3	11,28	0	+	=	=	=		✓
4	13,03	0	+	+	+	=		✓
5	17,39	+	+	+	+	+		✓
6	17,53	+	+	+	+	+		✓
7	18,90	+	+	+	+	+		✓
8	19,76	+	+	+	+	+		✓
9	20,99	+	+	+	+	+		✓
10	21,39	+	+	+	+	+		✓
11	21,91	0	+	+	+	+		✓
12	22,35	+	-	-	-	-	✓	
13	23,64	0	+	+	+	+		✓
14	24,69	+	-	-	-	-	✓	
15	25,17	+	+	+	+	=		✓
16	26,96	0	+	+	+	=		✓
17	29,03	0	+	+	+	+		✓
18	31,03	+	-	-	-	=	✓	
19	32,74	+	+	+	+	=		✓

In order to further confirm the obtained results, the total acid number (TAN) was determined for both the fresh oil and the oil exposed to 180ºC for 440 hours, following the protocol expressed in ASTM D 974-04 (Standard Test Method for Acid and Base Number by Color-Indicator Titration). The values obtained were 0.226 mgKOH/g and 1.11 mgKOH/g, respectively. Therefore, there were some acidic compounds produced over the 440 hours of experiment, which were not detected in the FTIR. However, this slight bump in the TAN is not that significant. Therefore, considering this information and the trends observed on both the HPLC and FTIR, it is safe to conclude that the commercial oil had an effective additive package, able to prevent its degradation for a significant amount of time.

4.2.2. Single-additive antioxidant containing lubricant

4.2.2.1. The role of DODPA

The specific neopolyol ester, which is the base of the commercial oil, was tested, with only DODPA, with PAN only and by itself with no additives, under the same conditions as the commercial oil.

Once again, by observing the FTIR, it is clearly visible that DODPA is an effective antioxidant, since the obtained spectra are constant and similar to those of the commercial oil, except for time 440h. At this time a clear shift of the main bands can be observed, which indicate that the oil's esters have started to undergo oxidative degradation.

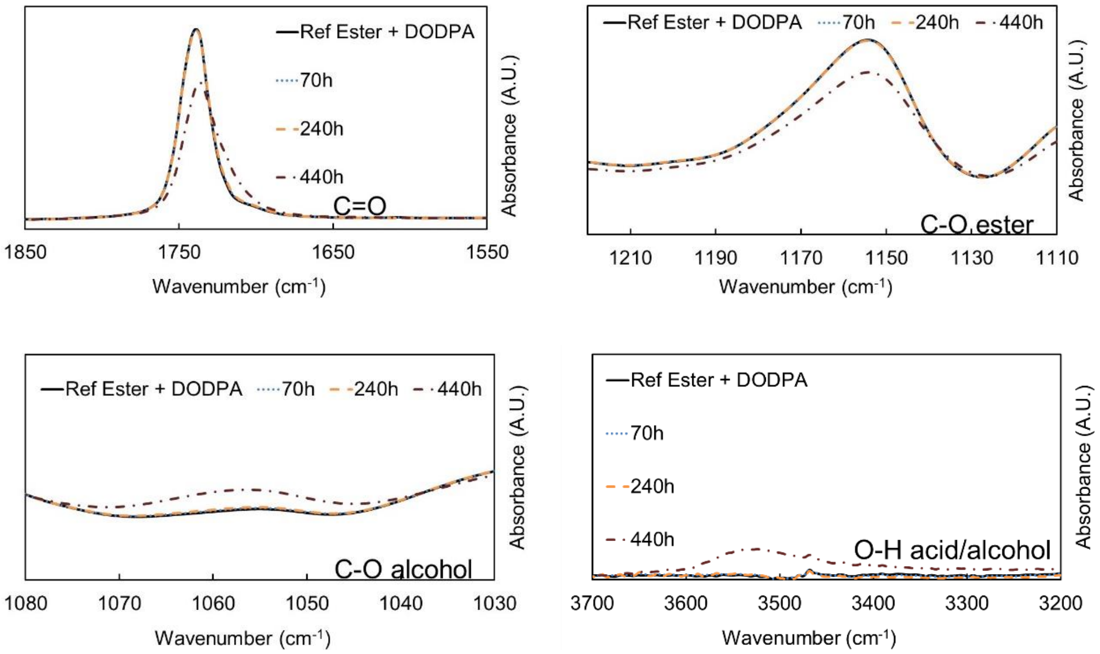


Figure 14 - FTIR analysis for the ester base stock with DODPA as the only additive.

The onset of this degradation can be understood by the consumption rate of the DODPA antioxidant, seen in Figure 12, as by time 440h the DODPA has been almost entirely depleted and the remaining amount is not enough to prevent the oxidation of the esters. This degradation is confirmed by the great increase in the TAN from 0.028 mgKOH/g, of the fresh ester with DODPA, to 13.9 mgKOH/g of the 440 hours sample.

Once more, assuming a first order kinetic model, as in the commercial oil, it is possible to obtain an expression for the consumption of DODPA with time and its kinetic constant.

$$C = 100 \times e^{-0.006t} \tag{3}$$

Therefore, from equations (2) and (3), the kinetic constants for the commercial oil and the ester base oil with only DODPA are 0.003 and 0.006h^{-1}, respectively. Hence, the kinetic constant for DODPA when employed alone in the ester is two times bigger than in the commercial oil, translating in a much faster consumption of DODPA. This phenomenon can be attributed to the synergistic effects of the other additives present in the commercial oil, like for example with PAN [22], [23], or interactions amongst multiple additives can lead to antioxidant behavior, delaying the consumption of DODPA.

Furthermore, once again, as observed in the commercial oil, a link between a decrease of the consumption rate of DODPA and the onset of the intermediate by-products can be observed by comparing Figure 12 and Table 3, further confirming the hypothesis that DODPA produces active antioxidant products. Posterior changes in the slope of the consumption of DODPA with time, can be attributed to a boost in the consumption of these products, as well as to the lower concentration of DODPA present, reducing the probability of occurring DODPA related reactions.

As for the HPLC results, only 7 products were detected. However, they indicate that there are at least some similarities in the reaction mechanisms of DODPA by itself and in the commercial oil, as in both chromatograms, 3 products were detected with very similar retention times, meaning that they are probably the same, these were products 2, 4 and 6 of the oil with only DODPA and products 8, 10 and 15 of the commercial oil, respectively. Since there is a slight change in the behavior of the oil, some other products of DODPA could have been produced, at different time frames, but were not detected due to the different rates of consumption of DODPA. The diverging results could also be attributed to the fact that the commercial oil has additional additives, which could interact amongst themselves, as previously stated.

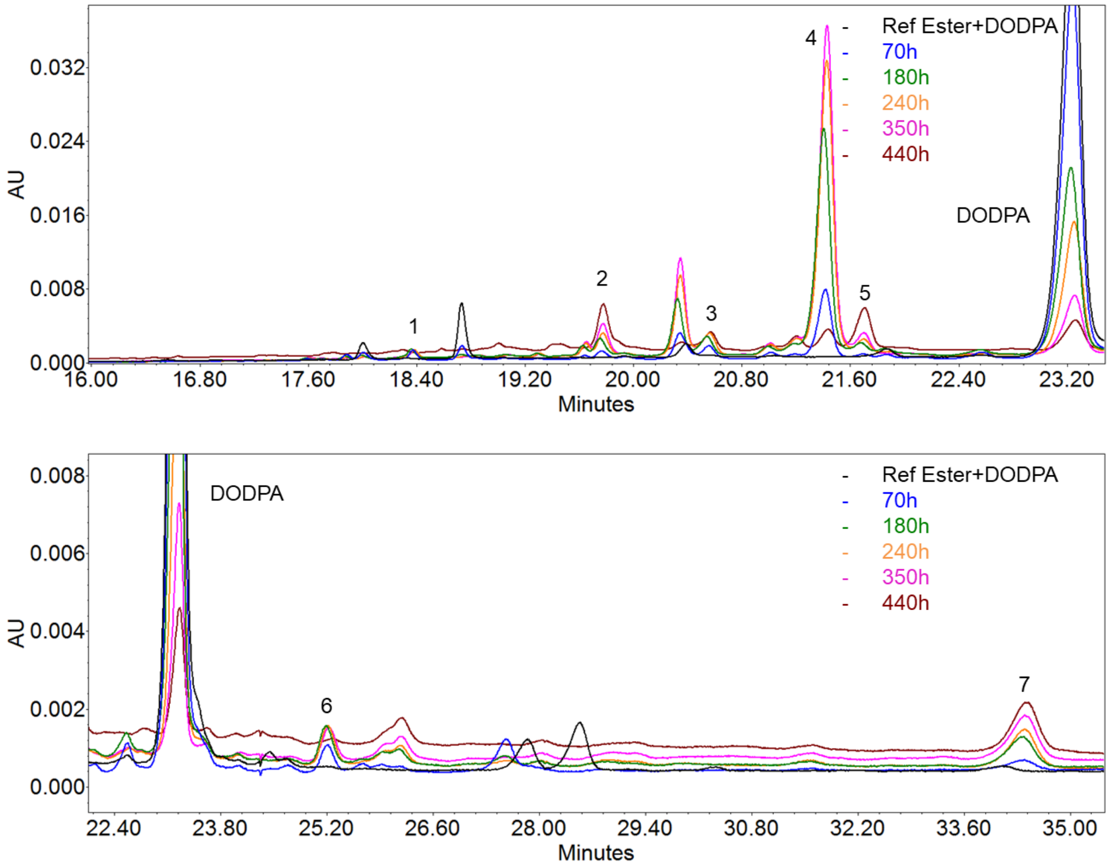


Figure 15 - HPLC chromatograms obtained for the ester base stock with DODPA as the only additive.

Table 3 - Overall fluctuation of the HPLC peaks for the different products of the ester with DODPA as the sole additive. Products 2, 4 and 6 had similar retention times and were determined to be the same as products 8, 10 and 15 of the commercial oil's HPLC.

Peak n°	Retention time (min)	70 h	180 h	240 h	350 h	440 h	Type of product	
							Intermediate	Final Product
1	18,37	+	+	-	-	-	✓	
2	19,79	+	+	+	+	+		✓
3	20,56	+	+	+	-	-	✓	
4	21,44	+	+	+	+	-	✓	
5	21,69	+	+	+	+	+		✓
6	25,23	+	+	+	-	-	✓	
7	34,44	+	+	+	+	+		✓

It is interesting to note that when the oil is aged on a PetroOxy device [35], the consumption of DODPA by itself is slower than in the commercial oil, which is contrary to the results shown in this study. However, the phenomenon observed in the thin-film metal plate was more in accordance with what would be expected, once again, as previously mentioned, the synergistic interactions between additives would lead to a slower consumption rate of DODPA.

4.2.2.2. The role of PAN

When analyzing Figure 12, it is visible that, unlike DODPA, the consumption of PAN was, probably, not influenced by the other additives in the commercial oil, as a similar rate of consumption for PAN on its own in the ester base and in the commercial oil is observed, it is depleted at around 100h. Nevertheless, at the 70h mark, the remaining amount of PAN in the commercial oil is smaller than that of when it is employed on its own. This most probably is due to an additional consumption of PAN due to synergistic effects between this antioxidant and other additives present in the oil's additive package. This phenomenon is most likely due to PAN's interaction with DODPA, where it has been shown that it is consumed sacrificially towards the regeneration of DODPA [22]. However, to further comprehend the phenomenon in hand, further experiments should be conducted. It would be interesting to repeat these experiments with a focus on the first 70 hours of the experiments' time frame, in order to fully understand the kinetics of PAN's consumption.

Furthermore, the contrasting results for the antioxidants clearly show that PAN is consumed much faster than DODPA, which translates in an earlier onset of the ester's degradation, as it is visible in the FTIR results obtained, Figure 16. There are clear shifts in the main bands of the spectra, especially in the O-H acid/alcohol band, at around 3500 cm^{-1}, which shows a slight bump even at time 70h. This greater deterioration of the ester base stock is confirmed by an increase, with time, in the TAN from 0.028 mgKOH/g to 23.7 mgKOH/g.

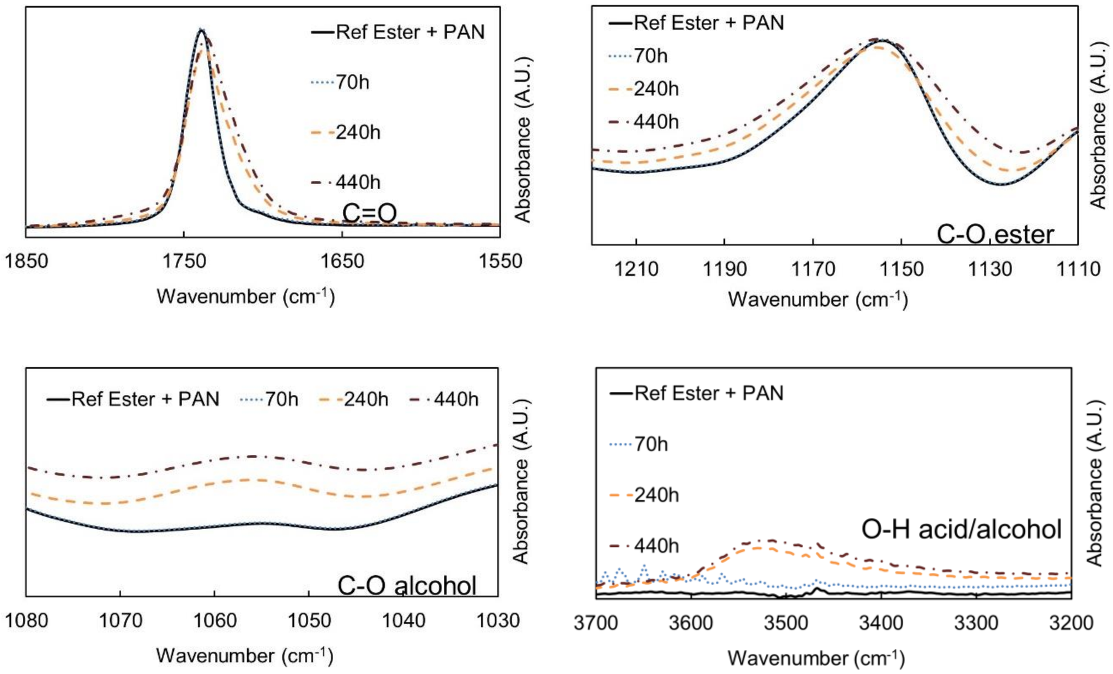


Figure 16 - FTIR analysis for the ester with PAN as the sole additive.

The FTIR results show that PAN, for the most part, is an effective antioxidant, as it was able to delay the oxidation processes by around 70h, however it is consumed extremely quickly, therefore, unlike DODPA, it was not possible to confirm if PAN is able to produce products which also act as antioxidants, as it was not possible to detect potential PAN intermediate products in the HPLC chromatogram, Figure 17. Additionally, in total, only four products were detected in the HPLC, at 70h. For the remaining times, the chromatograms obtained were uncharacteristic, as the PAN was completely consumed and there was nothing to be detected by the HPLC analysis.

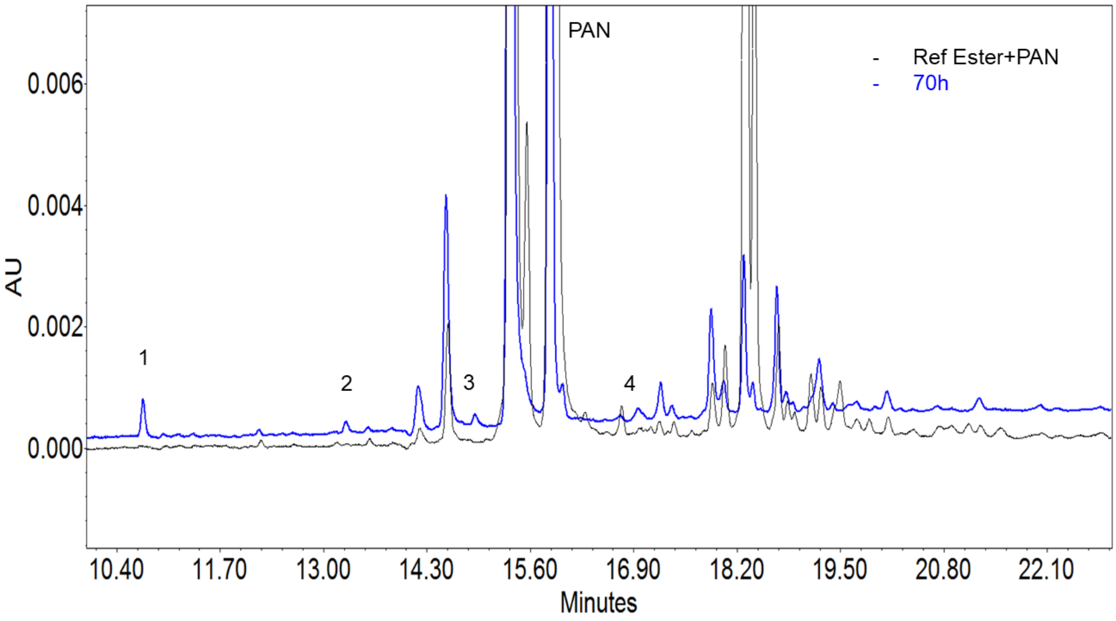


Figure 17 - HPLC chromatogram for the ester base stock with only PAN as an additive.

Table 4 – Retention times of the products detected on the HPLC for the ester base stock with PAN as the sole additive.

Peak n°	Retention time (min)
1	10,76
2	13,27
3	14,90
4	16,96

4.2.3. Oxidation stability of the neopolyol ester base oil without additives

Figure 18 shows the FTIR results obtained. By analyzing these and comparing with the remaining results, it becomes evident that the antioxidants have a very important role in the prevention of the oil's degradation and in its preservation, as without additives the FTIR spectrums obtained fluctuate considerably, when compared to the consistency of the FTIR of the commercial oil.

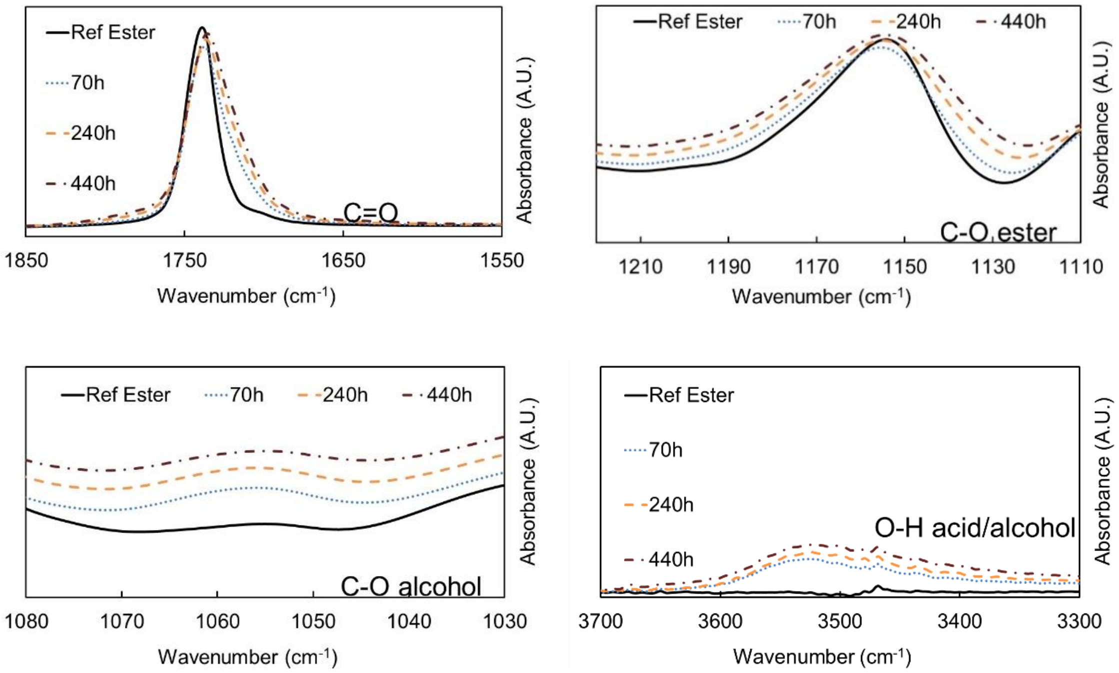


Figure 18 - FTIR analysis of the ester base stock.

There is a clear consumption of ester in the first moments of oxidation, seen in the C=O and C-O ester bonds' peaks (1740 and 1155 cm^{-1}, respectively), as they are lower at 70h. The ester is being consumed and produced alcohols and acids, corroborated by the C-O alcohol and O-H acid bonds' peaks (1055 and 3500 cm^{-1}, respectively) increasing. As the experiment progressed alcohols and acids continued to be produced, but these react amongst themselves, visible in the slower increase of the peaks. On the other hand, the depletion of esters is slower than the production of new esters, ketones, aldehydes and acids, as the C=O bond peak rises with time, after the 70h mark.

These results diverge from those obtained in a PetroOxy device [35], in which the oil is subjected to harsher conditions, forcing the oxidation process. While in the PetroOxy study [35] there was no acid nor alcohol formation and a decline in the C=O ester peak, in this experiment, as previously stated, there was an apparent net gain in C=O bonds and a clear formation of alcohols and acids, which is closer to what one would expect.

Nonetheless, overall, this sample was the one that suffered the most severe degradation over the experiments time frame. This is clearly seen in the TAN, as it went from 0.051 mgKOH/g when the oil was fresh, to 32.2 mgKOH/g, after 440 hours.

Chapter 5

Conclusions and Future Work

The work's main conclusions are summarized in this chapter. Additionally, some suggestions on future improvements and potentially interesting fields to research are done.

Overall, the experimental procedure, through the analysis, was shown to be successful in providing a glimpse of what occurs in the oxidative degradation of aircraft engine lubricants.

In this study, it was possible to conclude that the antioxidant packages employed in commercial oils are effective in preventing the oil's degradation and help maintain its properties, as long as they are present in the oil in adequate amounts. It was also possible to check that DODPA is a longer lasting antioxidant than PAN, as they act through different mechanisms, however they are more effective when employed together, which corroborates some findings in literature [22]. Even though the production of antioxidant intermediates in the commercial oil is most probably linked to both PAN and DODPA, it was only possible to confirm this phenomenon for DODPA, given the fact that PAN was consumed too quickly, therefore the window of opportunity to observe this was quite small. Additionally, it was possible to observe the existence of synergistic antioxidant effects between the additives employed in the commercial oil, since these effects were not found when the antioxidants were used independently in the neopolyol ester-base.

It is also interesting to note that the results obtained from this experimental setup was closer to the expected degradation consequences of a real-life engine, when compared to those obtained in the PetroOxy device [35], an enhanced oxidation test. This is especially visible in the FTIR results, which show the appearance of bands linked to the development of acids and alcohols, expected products from the oxidative degradation of esters, which did not appear on the PetroOxy samples. However, the greatest drawback of this experimental procedure is the fact that they are highly time consuming when compared to the PetroOxy

Therefore, even though it was possible to obtain an interesting insight into the degradation of the neopolyol-based lubricating oil, there is still a lot of work to be done on the field and on the spectrum of the work developed in this thesis. It would be interesting to test the synergistic effects of the additives amongst themselves. First of all, testing the ester base with both PAN and DODPA as the sole additives would provide an insight into if there are any other additives in the commercial additive package that work synergistically to prevent the oil's oxidation, this could be done by comparing DODPA's kinetics in every scenario. Other possibly interesting fields to study are the influence of other additives on the antioxidative capability of the additive package, especially the influence of TCP, and the influence of the operating conditions, such as the top-up mechanism.

Implementing a mass spectrometer alongside the HPLC would be an interesting investment, as it could give greater certainty in what by-products and intermediates are produced during the ageing process, as it would provide pivotal information to identifying the detected products.

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