

Abstract

The oxidation of a synthetic aircraft engine lubricant was studied using a laboratory scale thin film plate. Therefore, a neopolyol ester lubricant was oxidized in an open cylindrical stainless-steel container, under 180°C, 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. Furthermore, the consumption of the antioxidants with time was also obtained, as well as the kinetics for one of them. Additionally, these results were also compared to those obtained for an accelerated oxidation test, in a PetroOxy device.

Key-words: lubricant, neopolyol ester, antioxidant, oxidation stability.

Abbreviations: FTIR – Fourier Transform Infrared Spectroscopy; HPLC – High Performance Liquid Chromatography; PAN – phenyl-1-naphtylamine; DODPA – dioctyldiphenylamine.

1. Introduction

As aircraft engines evolve to become more efficient and powerful, the operating conditions of these engines become harsher and harsher, meaning the conditions, to which lubricating oils are exposed to, are progressively stricter, aggravating their degradation. Furthermore, there is a concerted effort to reduce the consumption and the replenishing of lubricating oils. Therefore, in order to keep up with this ever evolving and demanding industry, it is pivotal to have a greater understanding on how lubricating oils degrade with time [1]–[3].

One of the greatest factors contributing to the degradation of these oils is the process of radical oxidation [4]. When the synthetic neopolyol ester-based oil is exposed to high temperatures and oxygen, the ester molecules break down forming free radicals, hence undergoing the initiation step [5], [6]. The initiation step is followed by the propagation, autocatalytic and termination steps. In these steps the radicals react with the other ester molecules, oxygen molecules, between themselves or with product molecules from other radical reactions, forming a wide array of products, such as carboxylic acids, aldehydes, ketones, alcohols and other esters [5], [7]. This four-step oxidation mechanism is schematically represented in Figure 1.

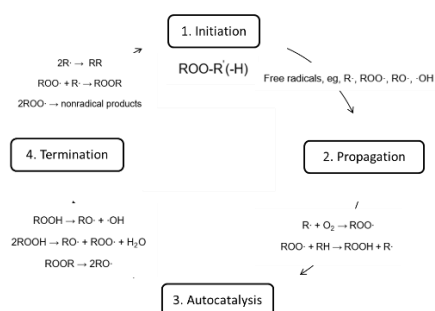


Figure 1 - Schematic representation of the radical oxidation mechanism.

In order to counteract this degradation, antioxidants are employed [7], [8]. These can either work by trapping the free radicals or by decomposing peroxides, these are known as primary and secondary antioxidants, respectively [7]–[9]. Even though there is an attempt to develop new

ecofriendly antioxidants [10], phenyl-1-naphtylamine (PAN, C16H13N) and dioctyldiphenylamine (DODPA, C28H43N) remain as the main antioxidants used in the aeronautic industry, they are both secondary aromatic amines. They are both primary antioxidants and work by disrupting the propagation step, by donating the hydrogen of their N-H bond, which is particularly susceptible to attacks from the peroxy radicals. The free electron in their structure, due to the loss of the hydrogen, is kept stable by their ring structure [11], [12].

Contrary to the work already conducted on neopolyol oxidation, this study is the first dealing with the degradation of the neopolyol ester-based oil in a static environment using a laboratory scale thin film metal plate, instead of forcing the oxidation to occur under harsh conditions and in an accelerated fashion in a specific device [13], [14] or in a static glass laboratory container [15]. This study attempted to obtain a more realistic window into the degradation of jet engine lubricating oils, when compared to the remaining work developed in this field.

As for the analysis of the samples obtained, high performance liquid chromatography (HPLC) and Fourier transform infrared spectroscopy (FTIR) were used.

2. Materials and Methods

2.1. 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 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.

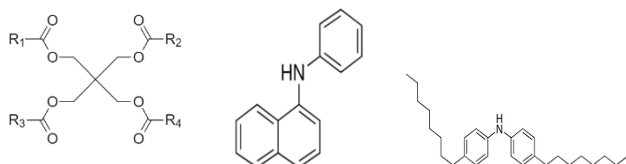


Figure 2 - Molecular structure of the oil's main components, the neopolyol ester (left), PAN (middle) and DODPA (right).

2.2. Oxidation Tests

The oxidation test was conducted on an open stainless-steel cylindrical container. 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 180°C. 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.

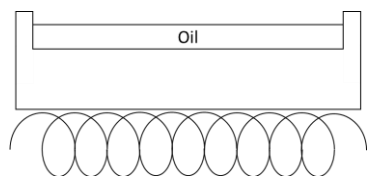


Figure 3 - Schematic representation of the oxidation test.

2.3. 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 μ L volume of this solution was then injected into a stainless-steel column (Waters XSelect type CSH C18, 250x4.6 mm ID, 5 μ m 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 5 shows a typical chromatogram of the lubricant before ageing. One peak at a specific retention time corresponds to one specific molecule. In this case, phenyl-1-naphthylamine (PAN) is detected at 15.75 min, and dioctyldiphenylamine (DODPA) at 23.24 min.

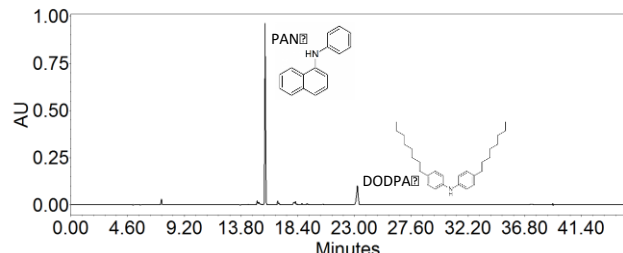


Figure 5 - HPLC chromatogram of fresh oil. Retention time of the additives: phenyl-1-naphthylamine (PAN) 15.75 min; (middle); (right) dioctyldiphenylamine (DODPA) 23.24 min.

2.4. 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} [16], [17], whereas C-H bonds, i.e. C-H2, C-H3 can be observed at about 3000 cm^{-1} respectively [16], [17]. The analysis of the FTIR spectra, therefore, allows for the detection of the 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) [16], [17]. This can be observed in Figure 4.

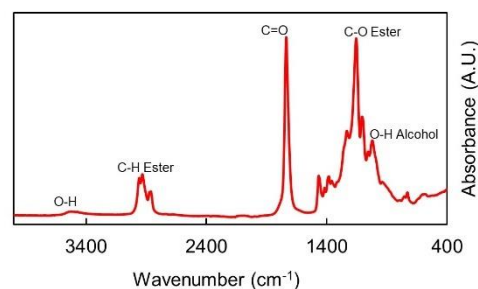


Figure 4 - FTIR of oxidized oil. Chemical bonds focused and their respective wave numbers: acid O-H bond at 3500 cm^{-1} , ester C-H bonds at around 3000 cm^{-1} , ester C=O bond at 1710 cm^{-1} , ester C-O bond at 1200 cm^{-1} and alcohol O-H bond at 1050 cm^{-1} .

3. Results and Discussion

3.1. Thermo-Oxidative Degradation of a Commercial Oil

By analyzing the FTIR results, shown in Figure 6, 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.

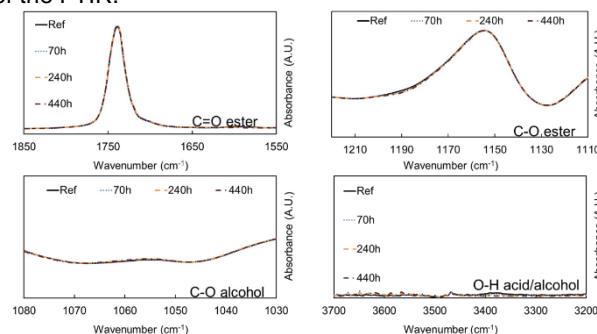


Figure 6 - FTIR analysis for the commercial oil.

As for the antioxidants present in the oil, their consumption can be analyzed in the HPLC results, shown in Figure 8. From these, it was possible to extrapolate the % consumption of the antioxidant additives over time, shown in Figure 7. 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.

Assuming DODPA follows a first order kinetic model, it

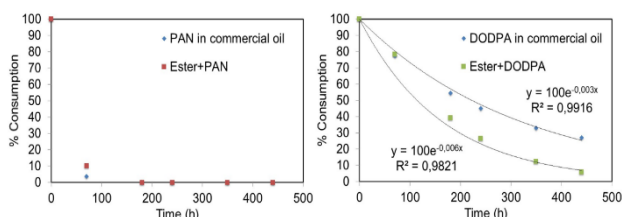


Figure 7 - The consumption of both PAN and DODPA as a function of time, both in the commercial oil and as solo additives in the ester base stock.

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 1. 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 [9], [11]. 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.

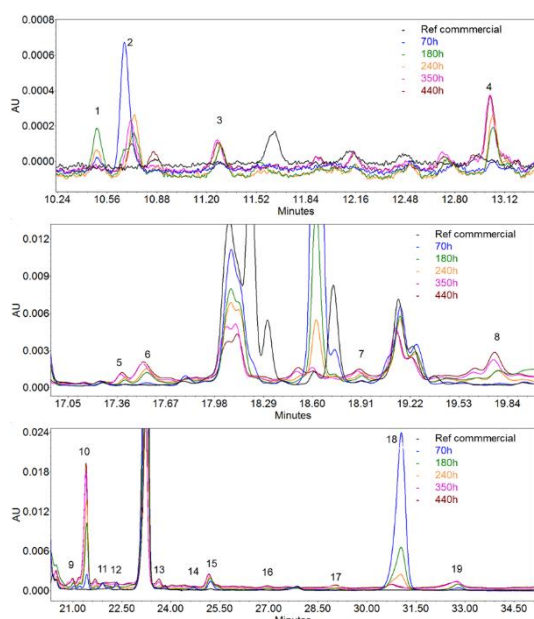


Figure 8 - HPLC chromatograms for the commercial oil.

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 180°C 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.

Table 1 - 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	+	+	+	+	=		✓

3.2. Single Additive Antioxidant Containing Lubricant

3.2.1. DODPA's Role

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.

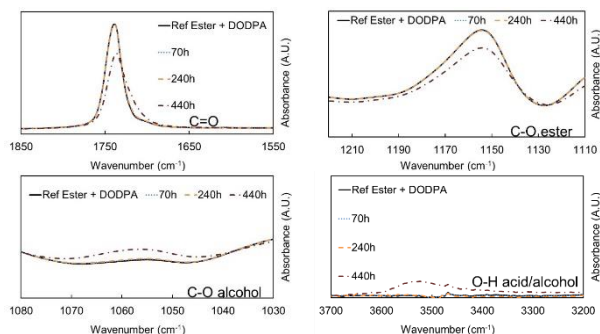


Figure 9 - FTIR analysis for the ester base stock with DODPA as the only additive.

The onset of this degradation can be understood by the consumption rate of the DODPA antioxidant, seen in Figure 7, 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.

$$C = 100 \times e^{-0.006t} \quad (3)$$

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 [11], [18], 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 7 and Table 2, 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.

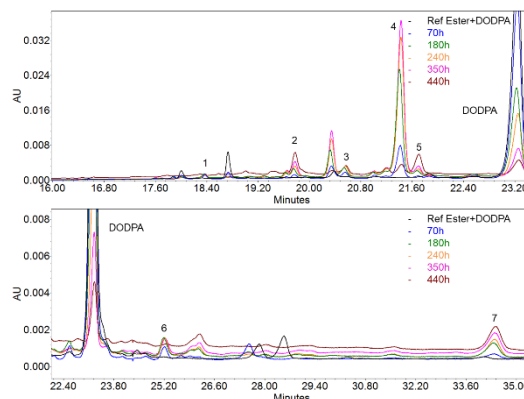


Figure 10 - HPLC chromatograms obtained for the ester base stock with DODPA as the only additive.

Table 2 - 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 [13], the consumption of DODPA by itself is slower than in the commercial oil, which is contrary to the results shown in this article. 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.

3.2.2. PAN's Role

When analyzing Figure 7, 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 11. 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.

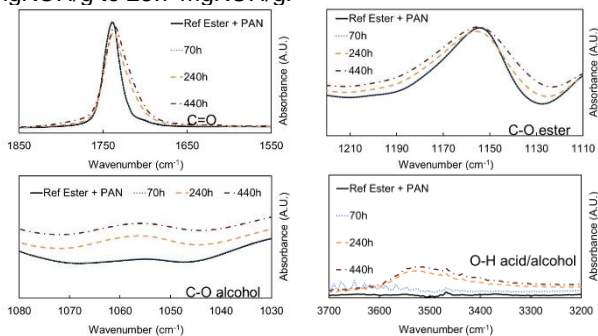


Figure 11 - FTIR analysis for the ester with PAN as the sole additive.

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 can produce products which also act as antioxidants, as it was not possible to detect possible PAN intermediate products in the HPLC chromatogram, Figure 12. 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.

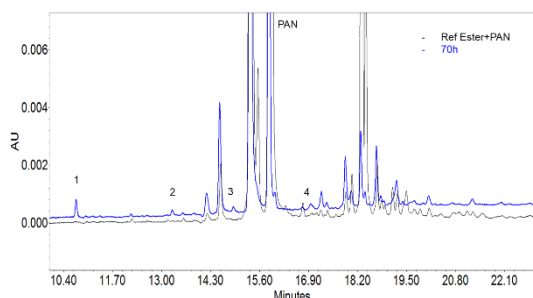


Figure 12 - HPLC chromatogram for the ester base stock with only PAN as an additive.

Table 3 – 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

3.3. Oxidation Stability of the Neopolyol Ester Base Oil Without Additives

Figure 13 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.

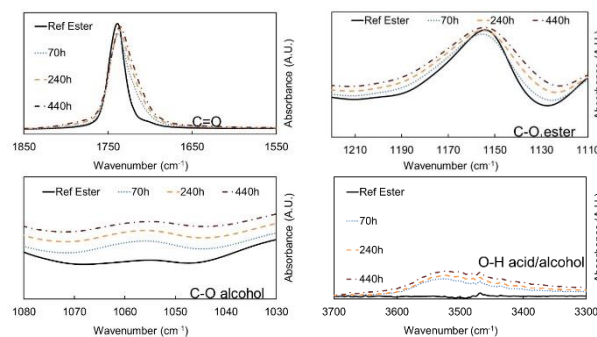


Figure 13 - FTIR analysis of the ester base stock.

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 [13], in which the oil is subjected to harsher conditions, forcing the oxidation process. While in the PetroOxy study [13] 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.

4. Conclusions

Overall, the experimental procedure and analysis studied in this article were able to show a glimpse into 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 oils degradation and maintaining 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 and that they are more effective antioxidants when employed together, which corroborates some findings in literature [11], [18]. 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.

Furthermore, when comparing the results obtained in this article with those of the PetroOxy device, it can be stated that the experimental procedure followed here is closer to what happens in a real-life situation, since the results obtained were, in general, closer to what one would expect. However, the greatest drawback of this experimental procedure is the fact that it is highly time consuming when compared to the PetroOxy [13].

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