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MoDTC friction modifier additive degradation. Correlation between tribological performance and chemical changes

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ABSTRACT: Due to the complexity of the processes, the degradation mechanisms of molybdenum dithiocarbamate (MoDTC)-containing oil are still not fully understood. In order to get a better understanding of how a MoDTC additive works at the molecular level, correlation between its chemical behaviour in the bulk oil during thermo-oxidative degradation and its ability to reduce friction has been investigated. The combination of using High-Performance Liquid Chromatography (HPLC), Fourier Transform Infrared Spectroscopy (FT-IR) and Mass Spectroscopy (MS) techniques has provided much detailed information about the complex chemistry involved in the degradation process.

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Finally, the link between MoDTC additive depletion and its effectiveness to lower the friction has been studied and a hypothesis on the chemical pathway followed by MoDTC during a thermo-oxidative degradation process has been proposed.

I. INTRODUCTION

An engine lubricant undergoes a range of chemical and physical changes during its lifetime and this can result in some loss engine performance, which can also impact the fuel economy. This impact on an oil's fuel economy together with other problematic such as corrosion, cleanliness, emissions etc. can be estimated by tests designed by the International Lubricant Standardization and Approval Committee (ILSAC), which introduced, starting from the GF-3 standard, a fuel economy retention fired engine test (test sequence VIB). With subsequent GF-4, GF-5 and the upcoming introduction of GF-6, the requirements will be regulated in an even more stringent way. In order to develop new lubricants formulation with enhanced durability characteristics the importance of understanding how and why modern additives become unsuitable for their intended purpose is clearly evident The potential role of molybdenum dithiocarbamate (MoDTC) additive in promoting the energy efficiency, reducing the friction coefficient under boundary lubrication conditions in automotive engines is well known and this makes the evaluation of its performance very important. It has already been reported that this friction modifier has extremely good tribological performance [1-4]. However, the performance loss of MoDTC-containing lubricants due to oil degradation has also been published [12] and it remains unclear how the MoDTC behaves when subjected to ageing. For this reason more work needs to be done in this area before any conclusions can be made. To date, several investigations have been undertaken to determine the parameters effecting MoDTC friction reduction [1,2] and hypotheses [3, 4] have been made for mechanisms occurring inside the tribological contacts. All these studies provide strong support to the theory that the formation of layered molybdenum disulphide (MoS_2) material is the main mechanism governing the friction reduction whereas the presence of hard molybdenum trioxide (MoO_3) on the rubbing surfaces tends

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to deteriorate the friction and wear. However, due to the extremely complex chemical reaction paths of MoDTC molecules, the current understanding of its behaviour and the effect of its degradation on the tribological properties are still not fully identified.

To date the only investigations undertaken relating to the additive depletion evaluation on the bulk oil characterization have been performed using High-Performance Liquid Chromatography (HPLC). The authors, De Barros et al. [5], followed the MoDTC and ZDDP concentration during lubricant degradation process and hypothesized that the oxidation process significantly affects the exchange reaction supposed between MoDTC and ZDDP. The interaction of these two additives has also been analyzed by Kubo et al. [4]. The authors evaluated the effect of lubricant ageing on the friction reduction performance during engine testing. In this instance the remaining concentrations of zinc and molybdenum compounds were determined by HPLC, coupled with Fourier Transform Infrared Spectroscopy (FT-IR). It was shown that the addition of an antioxidant additive delayed the MoDTC depletion and consequently maintained the friction reduction over a longer time period. The synergistic effects between MoDTC and ZDDP and their lubricating performances have also been analyzed by Graham et al. [6]. Again, it has been confirmed that MoDTC additives can be protected against thermo-oxidative degradation by adding ZDDP additive. On the other side, these papers did not carry out the detailed bulk oil analysis to study the molecular behavior of MoDTC. For this reason additional investigations are clearly needed to further understand the MoDTC chemical reactions taking place during the degradation process and their impact on the friction reduction efficiency.

Recently, we presented the impact of the thermo-oxidative degradation of MoDTC-containing base oil on the tribological properties looking at the friction behaviour, the tribofilm morphology and its chemical composition [12].In particular, this work showed several differences between fresh and aged 1%wt MoDTC blended to base oil:

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- the fresh oil provided a significant reduction in friction coefficient over the full test duration, whilst when the oil was subjected to thermo-oxidative degradation, an induction time appeared which increased with the ageing time;

- by using XPS surface analysis the existence of two different molybdenum oxisulphide compounds in the tribofilm was hypothesized - $MoS_{2-x}O_x$ and $MoS_{2-y}O_y$ (where x<<y). The lower oxygen content compound was identified as responsible for the friction reduction. Indeed after 8 hours of ageing, the $MoS_{2-x}O_x$ concentration was very low and the friction coefficient was virtually identical to that of the additive free base oil.

Although XPS surface analysis was able to identify the chemical nature of the tribofilm, it was not possible to infer the decomposition mechanisms followed by MoDTC molecule using this single technique. Therefore, in this current work, we have extended our analytical strategy to obtain a deeper insight into the MoDTC friction modifier additive chemical changes under thermo-oxidative degradation. High-performance liquid chromatography (HPLC), Fourier Transform Infrared Spectroscopy (FT-IR) and mass spectroscopy (MS) have been included to follow the concentration of the remaining MoDTC and the nature of the decomposition products formed after the time-controlled degradation procedure. Finally the reaction pathway of a MoDTC additive when subjected to thermo-oxidative degradation is hypothesized.

II. METHODOLOGY

a. Additive and base oil

The chemical structure of MoDTC additive used in this work is shown in Figure 1. The additive used in this work is a mixture of different MoDTC molecules containing $4R=C_8$, $4R=C_{13}$ or $2R=C_8$ and $2R=C_{13}$. 1% by weight of this additive has been blended to a commercial mineral base oil grade III, as typically used in the lubrication of automotive motors.

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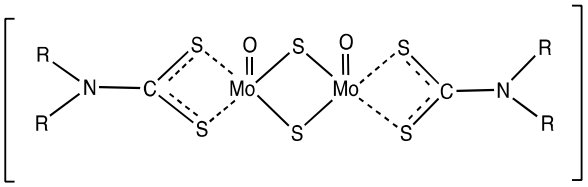

Fig 1. Chemical structure of the molybdenum dithiocarbamate (MoDTC) employed in this work. Note that it is presented a planar representation.

b. Degradation Procedure

The mixture of MoDTC in the base oil was degraded following the CEC-L-48-A00 standard. The samples have been heated up to 160°C using an in-house system consisting of a thermo-controlled heater and a round-bottom flask containing 300 mL oil sample. This is connected to a condenser in order to reduce the evaporation losses of the more volatile components. Samples were not exposed to any gas stream during the heating because the oxygen in the flask has been assumed adequate to allow the MoDTC degradation, although an inlet of air (or oxygen) would indeed speed up the ageing process.

For this study, additivated oil samples of 25 ml were withdrawn in steps of 1 hour up to a maximum of 8 hours of thermo-oxidative degradation.

c. High Performance Liquid Chromatography (HPLC)

A UHPLC system (Water Acquity) was used in reversed-phase mode, equipped with a module LC pump, auto-sampler and photodiode-array (PDA) detector was used. The HPLC parameters run according to TOTAL's internal procedure.

Samples were first weighed into a 100 ml vial and then diluted in heptane to obtain an oil/solvent ratio of ca. 1:20. Part of this solution was filtered through 0.2 μm micropore filter prior to analysis (in order to remove any particles present in the aged oil) and added in a 20 ml vial. At the end the diluted and filtrated samples were placed in autosampler racks. The area under the elution peak is used to determine the MoDTC concentration after a suitable calibration of the additive content.

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d. Mass Spectrometry (MS)

The Xevo G2 Q-TOF mass spectrometer was used both in positive and negative ESI mode for data acquisition and analysed the filtered fresh and aged oil. Typical source conditions for maximum intensity of precursor ions and the parameters set for the scan function used for the data acquisition were set according to TOTAL's internal procedure.

e. Fourier Transform Infra-Red Spectroscopy (FTIR)

Absorbance spectra were recorded with Nicolet 380 FTIR spectrometer, with 4 cm^{-1} resolution. The spectral range of the measurement set-up was to (4000-400) cm^{-1} with 30 scans. A background spectrum of the Potassium Bromide (KBr) window was taken before the measurement and automatically subtracted from the sample spectrum in order to obtain peaks related specifically to the lubricant sample (filtered oil).

III. RESULTS

a. Degraded oil: visual inspection

During the degradation process pronounced color changes- suggesting chemical modifications- were observed in all samples (Figure 2), The light green color of the freshly additivated oil (0 hours degradation time) became a darker green after 2 hours and the formation of solid-like black particles is clearly observed after 5 hours ageing time. If the oil was aged for longer time (8 hours), it became black.

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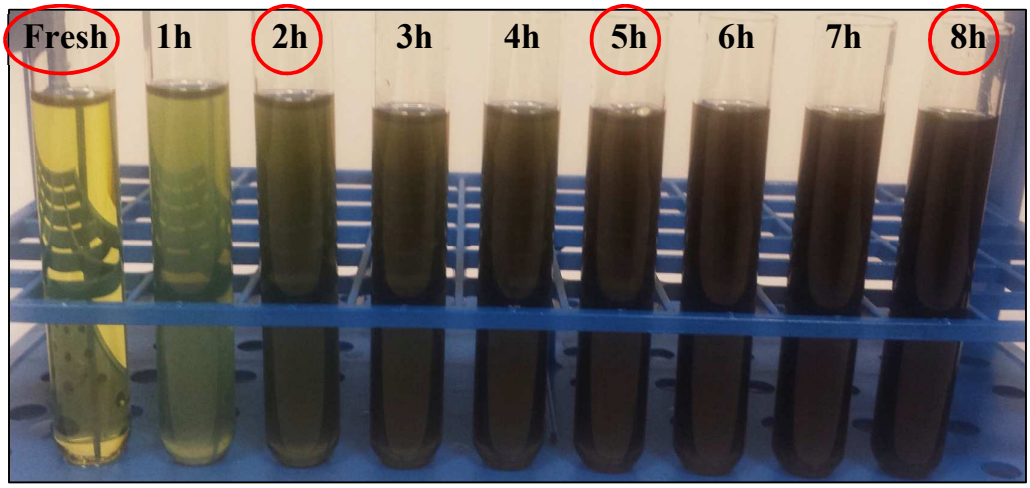

Fig. 2. MoDTC-containing base oil color changes with degradation time (0 hour to 8 hours ageing).

It was decided to carry out the tribological tests using the oil samples indicated in the figure 2 by the red circles for the key reasons as summarized in the Table 1.

Degradation Time (hours)	Observations
2	First changes in colour
5	Relevant formation of solid particles
8	Oil completely dark

Table. 1 Degradation time for the selected oil samples used in tribological tests.

b. Particles formation

As noted in Table 1, the degradation process of MoDTC additivated base oil leads to the production of black solid-like particles after short ageing time under our ageing conditions. After centrifuging the oils the changes in colour became much more apparent - see Figure 3. The chemical and morphological analysis of the particles, together with their impact on the friction behaviour will be reported in a separate paper.

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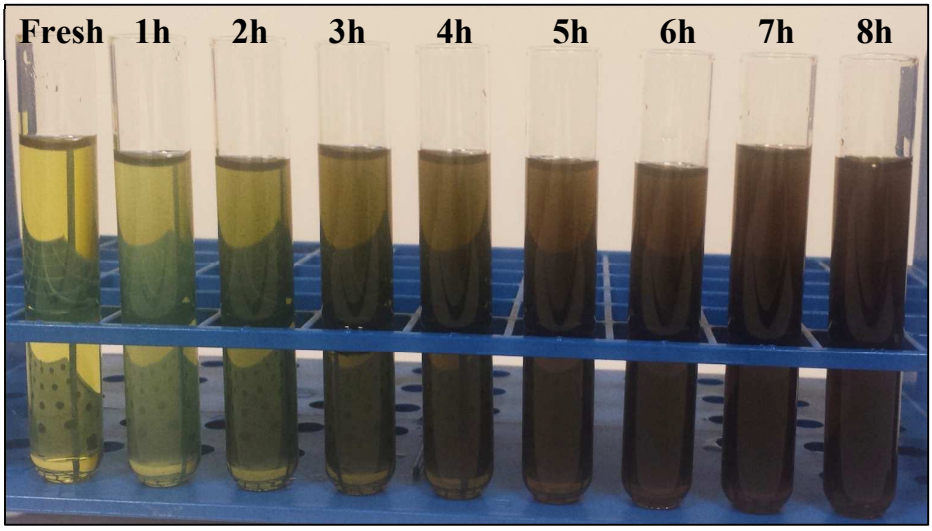

Fig 2. Degraded oils as a function of time. All samples have been centrifuged.

c. Influence of oil thermo-oxidative degradation on tribological properties

In our previous work [12] the lubricant ageing effect on the ability of MoDTC to lower the friction coefficient was investigated. Tribological tests with additivated base oil were acquired by a ball-on-flat type tribometer under reciprocating motion. The main result reported was the large increase in the friction coefficient obtained using MoDTC additivated base oil up to when the degradation process reached 8 hours ageing. At this point the friction reduction versus Base Oil became insignificant - this is shown in figure 4.

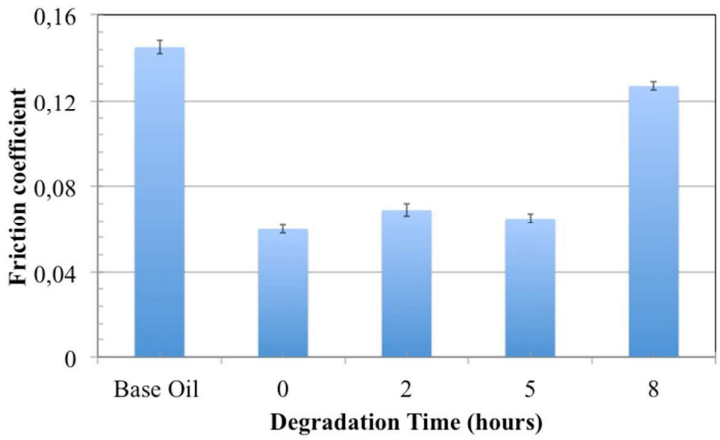

Fig 4. Steady-state friction coefficient values for the fresh and aged MoDTC-containing base oils [12].

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d. MoDTC additive depletion by High Performance Liquid Chromatography (HPLC)

The HPLC chromatograms for both fresh and aged oils are characterized by the presence of two peaks characteristic values of molybdenum dithiocarbamate additive. This is due to the two MoDTC alkyl chain length used in this work (hydrocarbon chain $4R=C_8$ or $4R=C_{13}$).

In order to accurately correlate the peak areas to the MoDTC concentration, calibration solutions with 8 different known concentrations in the mobile phase were prepared and injected in duplicate. Linear regression analysis was carried out on the curve generated by plotting the peak area response (x) versus the known concentration of MoDTC (y) expressed in ppm (Figure 5a, 5b).

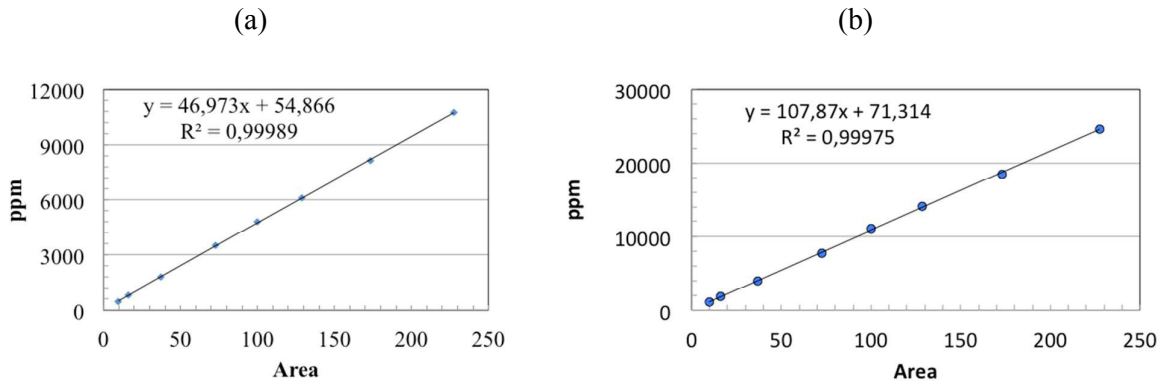

Fig 5. Calibration curves for MoDTC containing $4R=C_8$ (a) and MoDTC containing $2R_{13}$ and $2R_8$ (b).

The correlation coefficient (R^2= 0.9999) for the regression line demonstrates that there is a strong linear relationship between MoDTC concentration and the peak area.

Subsequently, experiments were carried out on 9 oils having 9 progressive degradation times, starting from 0 hours (fresh oil), over a period of 8 hours on every hour.

The presence of MoDTC in solution has been quantified by measuring the peak volume of the characteristic retention time for the two peaks for the MoDTC-containing base oil with the results plotted in Figure 6(a) and 6(b).

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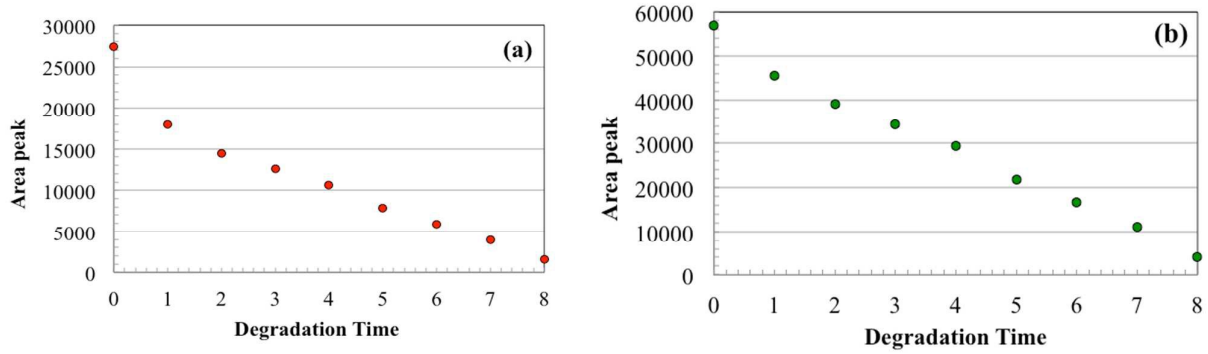

Fig 6. Additive depletion considering the MoDTC containing 4R=C_8 (a) and the MoDTC containing 2R_{13} and 2R_8 (b).

The presence of another small peak was detected and, in the same way, its areas were plotted as function of degradation time (Figure 7). The area of this peak seems to increase during the initial early degradation periods and then to gradually decrease. It is possible that a reaction product is formed in the beginning of the ageing process, followed by other chemical changes that lead to the consumption of this new compound. These results will be discussed more carefully within the next paragraph.

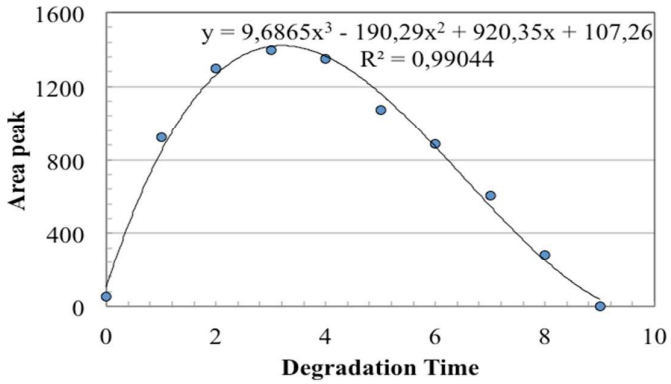

Fig 7. Additive depletion against degradation time taking in consideration the third new peak.

All the HPLC results relate to the fresh oil concentration at 100% and the MoDTC depletion is reported in percentage. The additive depletion of MoDTC additive, given by the sum of the two characteristic peaks is shown in figure 8. In the graph (C_{MoDTC_FRESH}) corresponds to the MoDTC

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concentration of fresh oil while the amount of remaining MoDTC in the base oil at the degradation time considered is called (C_{MoDTC}).

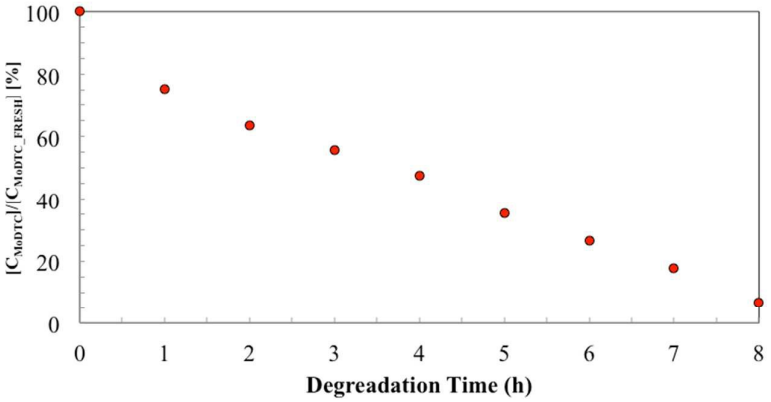

Fig 8. MoDTC additive depletion considering the sum of the two MoDTC characteristic peaks.

When the MoDTC-additivated base oil is aged, a linear reduction (kinetic zero order) of the MoDTC compound concentration is visible up to 8 hours degradation, at which point virtually all the MoDTC has become consumed.

e. Study of MoDTC molecular transformations by Mass Spectroscopy

Mass spectroscopy (MS) was used to obtain information about the molecular transformations of MoDTC present into the base oil and the degradation products formed during the ageing process. In order to ease the interpretation of the MS spectra, the fractional groups and their molecular weight- important for the understanding of the results presented in the current paper, are reported in the table 2.

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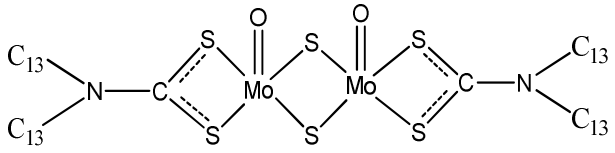
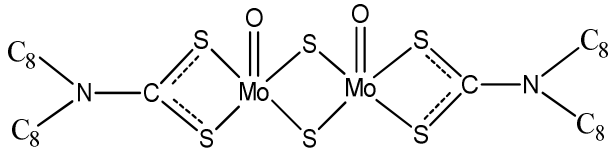
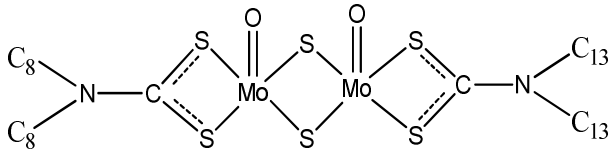
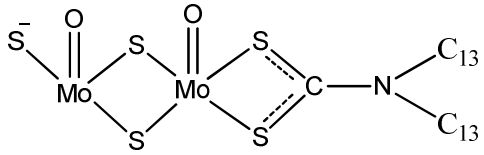
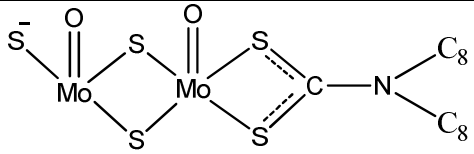
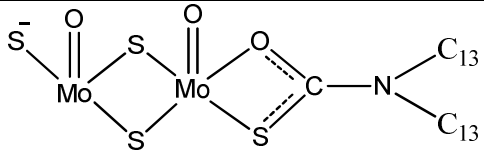
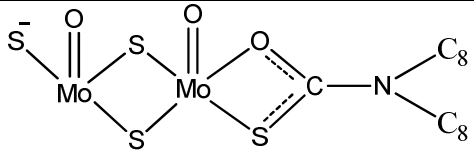
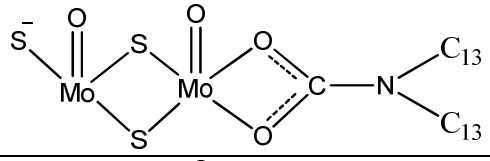
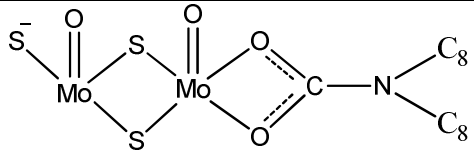
MoDTC molecules and fragments		MW
	Starting molecule having 4 R=C_{13}	1202
	Starting molecule having 4 R=C_8	922
	Starting molecule having 2 R=C_{13} and 2 R=C_8	1062
	Fragment A, having 2 radical group C_{13}	778
	Fragment B, having 2 radical group C_8	636
	Fragment C, having 1 sulfur atom replaced by an oxygen atom compared to the fragment A	762
	Fragment D, having 1 sulfur atom replaced by an oxygen atom compared to the fragment B	620
	Fragment E, having 2 sulfur atoms replaced by 2 oxygen atoms compared to the fragment A	746
	Fragment F, having 2 sulfur atoms replaced by 2 oxygen atoms compared to the fragment B	604

Tab. 2 MoDTC molecular fragments obtained by MS on degraded oils.

Considering that the radical group present in the MoDTC molecule analyzed in this work contains a mixture of hydrocarbon chains with C_8 and C_{13}, the MS results obtained using the positive mode

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confirmed the presence of MoDTC additive in the oils and the possibility to monitor its chemical change. In fact, the measured molecular weights observed in Figure 9 are in good agreement with the theoretical values presented in the table 5. In the same way, the m/z spectrum obtained analyzing the fresh sample under negative ionization conditions showed dominant ions with m/z at 636 and 778, which are consistent with the deprotonated molecular fragment (M-H-) (Figure 10).

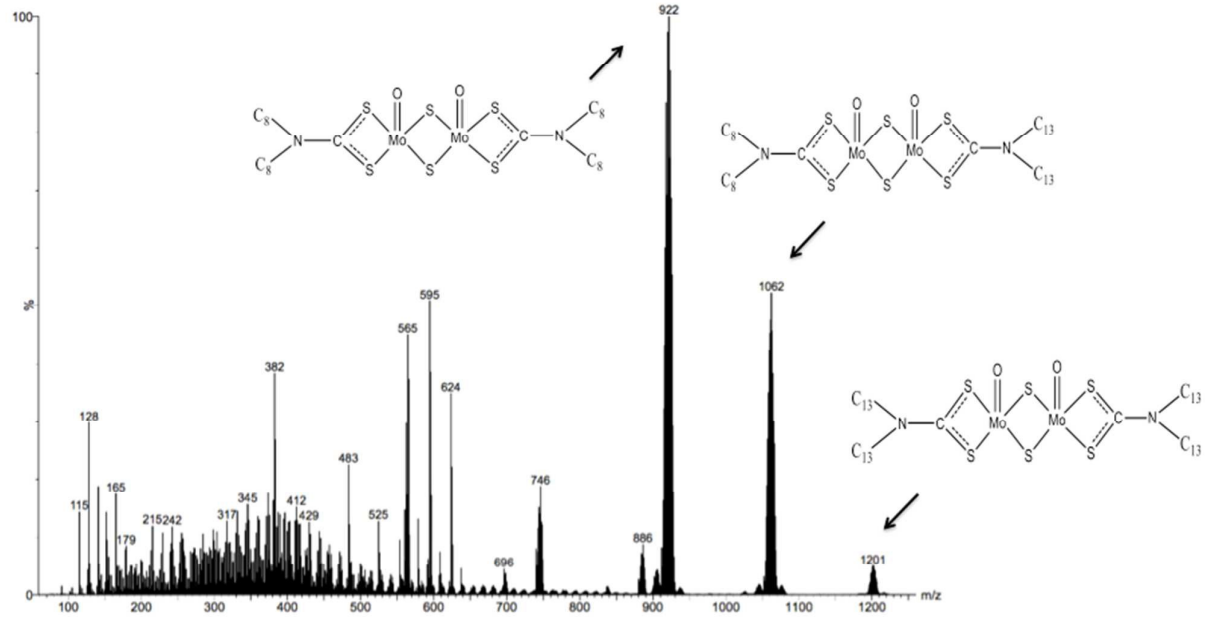

Fig 9. Mass spectrum obtained for fresh MoDTC-containing base oil in positive ion mode.

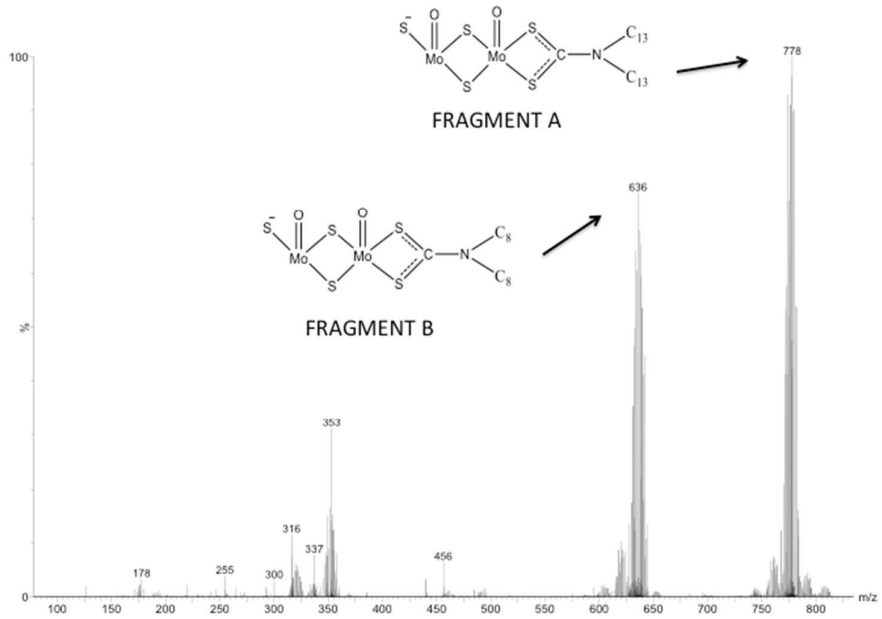

Fig 10. Mass spectrum obtained for fresh MoDTC-containing base oil in negative ion mode.

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Figure 11 shows the spectrometer for the oil aged for 1 hour. It is interesting to notice that the spectra relating to both fresh and aged oils contains other ion at m/z 762, thus 16 Da lower than the characteristic masses of MoDTC (Figure 11). These lower masses could be identified as the same molecular fragments but having sulfur atom (MW=32) replaced by an oxygen atom (MW=16). The same behavior is shown for the ion at m/z 636 (here not shown).

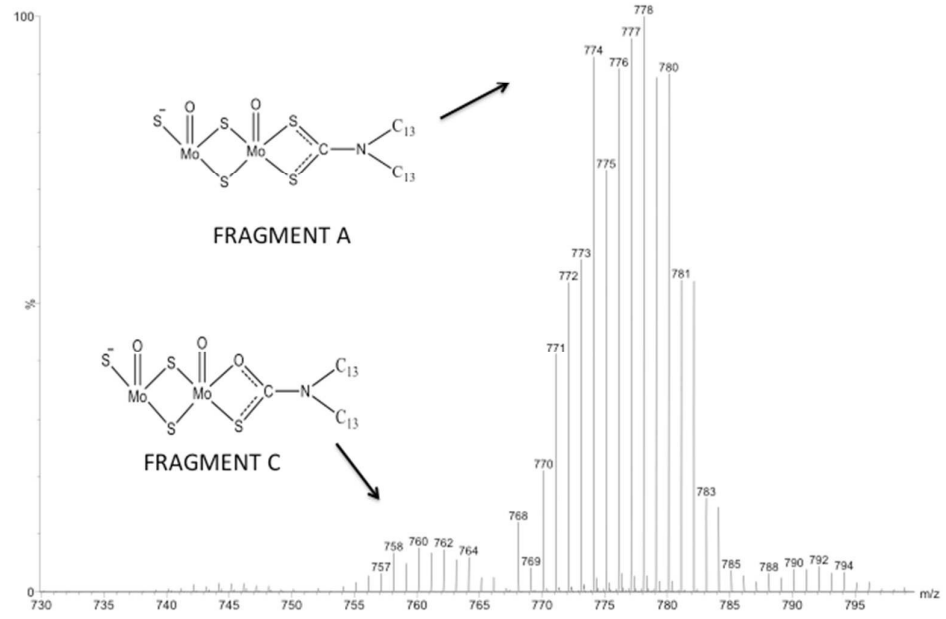

Fig 11. Mass spectrum obtained for 1h aged MoDTC-containing base oil in negative ion mode.

If the same analysis is extended to the full degradation period (Figure 12), it can be observed that after approximately 3 ageing hours, an additional reaction product peak appears, having 32 Da difference with the main peak. This trend is common to all the MoDTC fragments.

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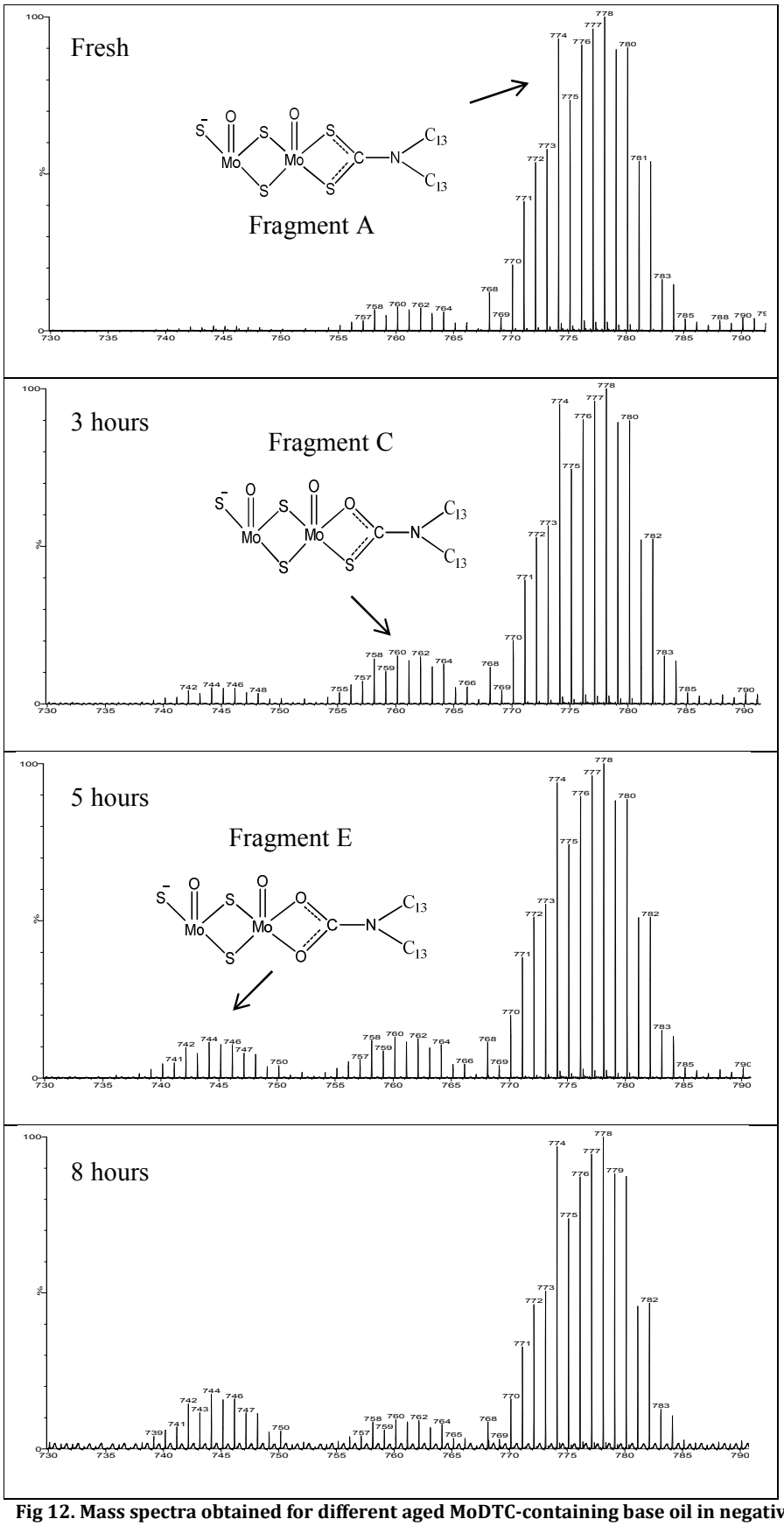

Fig 12. Mass spectra obtained for different aged MoDTC-containing base oil in negative ion mode

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In order to confirm assumption of the sulfur-oxygen replacement, the relative ratio between the main peak (I_{778}) intensity, corresponding to the molecular weight of the starting molecule fragment, and the sum (I_{762} + I_{746}) related to the other two reaction products peaks was calculated (Figure 13a).

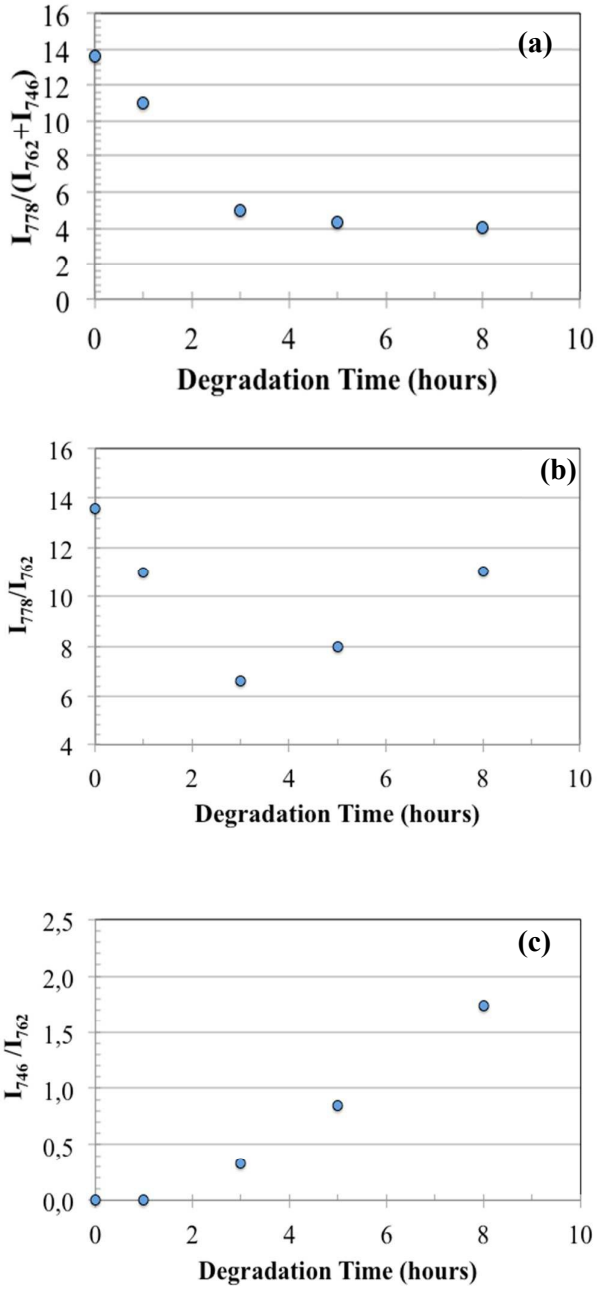

Fig 13. Relative ratio between (a) the main peak intensity (778 m/z) and the sum of the two reaction products (762 and 746 m/z); (b) the main peak intensity (778 m/z) and the first reaction product (762 m/z) intensity; (c) the second reaction product (746 m/z) intensity and the first reaction product (762 m/z) intensity.

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A marked reduction in the ratio value was obtained during the early ageing hours, confirming that the main fragment (778 m/z) is converting in the first reaction product (762 m/z), considering it is the only new species in the beginning of the degradation process. In other words, the results reported in figure 13 (a) suggests that when the degradation process starts, there is a decrease in the 778 m/z intensity peak (main fragment) and the intensity of new peak appeared (762 m/z) increases. For higher degradation time, the ratio value reaches a *plateau*, indicating that changes do not happen anymore in the additive molecule but in the first reaction product, which reacts giving the second reaction product (746 m/z). It appears that having one sulfur atom replaced by an oxygen atom the MoDTC molecule becomes more reactive to substitution by further oxygen compared to MoDTC itself.

The ratios (I_{778}/I_{762}) and (I_{746}/I_{762}) indicate the same behavior: in the Figure 13 (b) it is possible to see that when the oil starts to degrade, the main fragment (778 m/z) concentration decreases while the first reaction product with 762 m/z as molecular weight increases. Following the same line of reasoning, the first reaction product concentration after few degradation hours reacts giving the second reaction product with 746 m/z as molecular weight and, for this reason, the ratio in figure 13 (b) increases after 3 hours of degradation. Interpretation of Figure 13 (c) in the same way gives a coherent result: as the oil is degraded the increase of the second reaction product (746 m/z) -which is missing during the first ageing phase, is seen coincides with the decrease of the first reaction product (peak 762 m/z).

f. Study of MoDTC thermal-oxidative degradation by FTIR

Figure 14 shows the results of analysis of pure MoDTC diluted in base oil. The strong absorption bands seen within the area 2800-3000 cm^{-1-} corresponding to the C-H asymmetric stretch and C-H symmetric stretch of CH_2 and CH_3 bonds, originate from the base oil hydrocarbon structure [9]. These plus the absorbance bands relating to chemical bonds present in the MoDTC molecule are detailed on the graph in the absorption region 400 cm^{-1} -1600 cm^{-1} (Figure 15).

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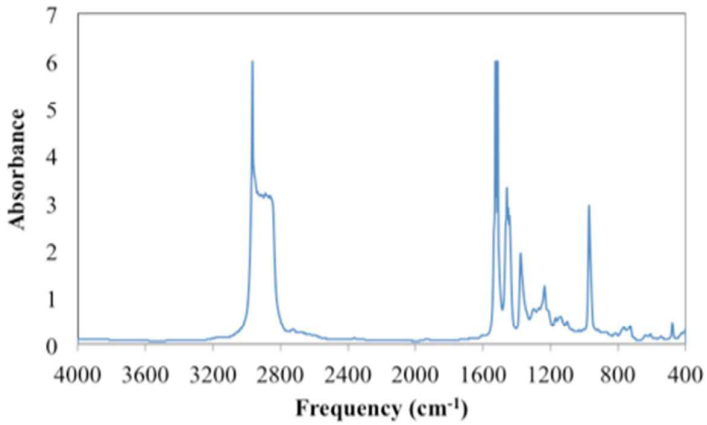

Fig 14. FT-IR spectrum of fresh pure MoDTC.

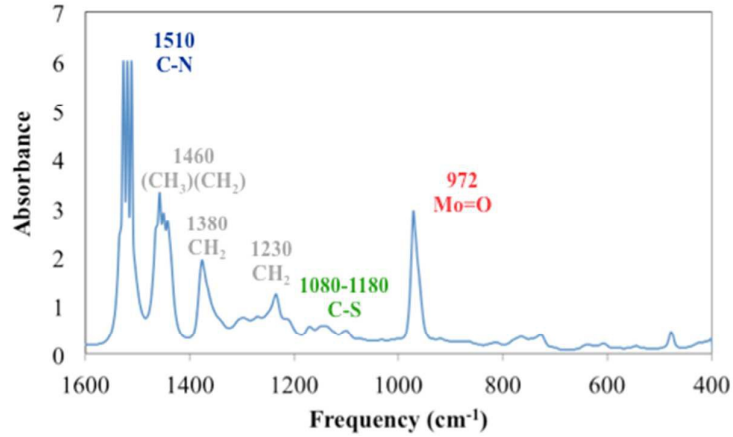

Fig 15. Zoom for the MoDTC FT-IR spectrum (400-1600 cm-^{1}).

The group of absorption bands assigned to the alkane chains lies at 1380 cm^{-1} and 1460 cm^{-1}. They originate from CH_3 umbrella bends, CH_2 scissors and the CH vibrational modes of branched and cyclic saturated chains [9].

The two typical absorption bands relating to the MoDTC compound are the one at 1510 cm^{-1} and at 972 cm^{-1}. The assignment of these bands has been already discussed in literature. A similar compound to the MoDTC studied in this work has also been analysed and the contribution at 1523 cm^{-1} has been attributed to the vibration of a partial CN bond in a CNS conformation [7]. However the same bands have been assigned also to a full C=N double bond [8]. The strong peak present at 972 cm^{-1} in this work was assigned to Mo=O, referring to previous studies [7].

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Subtraction spectra between fresh and aged oils have been calculated and they are plotted in Figure 16. These have been separated into two parts related to MoDTC characteristic peaks and a shift in y-direction has also been added for better clarity.

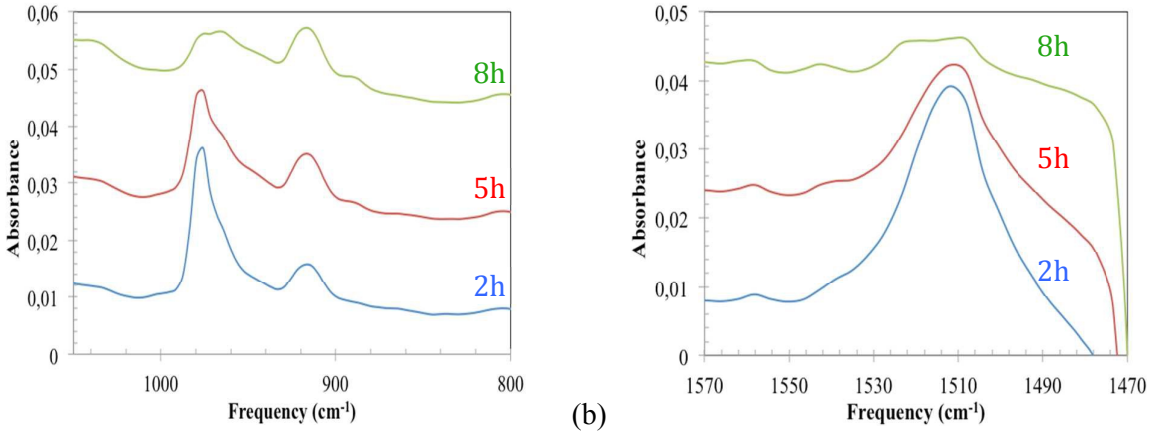

Fig 16. The resultant absorbance spectra after subtraction with the fresh oil in the area (800-1040) cm^{-1} corresponding to Mo=O (a) and (1470-1570) cm^{-1} corresponding to C-N bond (b).

IV. DISCUSSION

Comprehensive research into the bulk MoDTC-containing lubricant degradation has not yet been undertaken; understanding the MoDTC additive behaviour in lubricant base stock when subjected to thermal-oxidative degradation was clearly needed. Chromatographic and spectroscopic techniques were employed to establish the fundamental differences between the fresh and aged oils by monitoring the chemical changes during the degradation process.

As reported in the previous paragraph, 8 solutions of MoDTC additive in base oil with known concentration were analysed by means of liquid chromatography.

Considering the amount of MoDTC additive in the fresh sample to be 100% concentration, it has been possible to follow the additive depletion caused by the ageing process. The MoDTC almost completely disappeared from the oil after 8 hours and this result is exactly as anticipated given that no friction reduction was obtained when testing the aged oil.

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Previous works showed that the friction reducing property depends on the MoDTC concentration [1]. For this reason as the quantity of MoDTC in the oil is continually decreasing during oxidation (Figure 8), it was anticipated that the friction coefficient would also linearly increase. This theory is in disagreement with our previous results [12] where it was shown that employing 5 hours aged oil, after an induction time, the friction drops to the same low value obtained for the fresh oil (0.06). This suggests that the reduction in the friction value is not proportional to the MoDTC concentration; there is a minimum critical concentration required for achieving a low friction coefficient.

Using FT-IR technique, it was possible to obtain information about the chemical bonds present in the oil. The thermal-oxidative degradation process was found to impact the C-N and Mo=O peaks, the intensity of these bond peaks decreasing with the degradation time.

Detailed analyses for both fresh and aged oils by using mass spectroscopy has also revealed that during thermal-oxidative degradation there are chemical changes in the MoDTC molecule, and the most credible hypothesis indicates that this is the replacement of sulfur by an oxygen atom within the additive molecule. Additionally the difference between the peaks found in the chromatograms related to the aged oils is 16 Da, this is the difference between the sulfur molecular weight (32) and an oxygen atom (16). One further key item to note is that after a few degradation hours a second sulfur can be replaced by oxygen, this occurs in an easier way in comparison to the first reaction.

Consolidating all the data obtained from the HPLC, MS and FT-IR it is possible to hypothesize the chemical pathway followed by the MoDTC during thermal-oxidative degradation (Figure 17).

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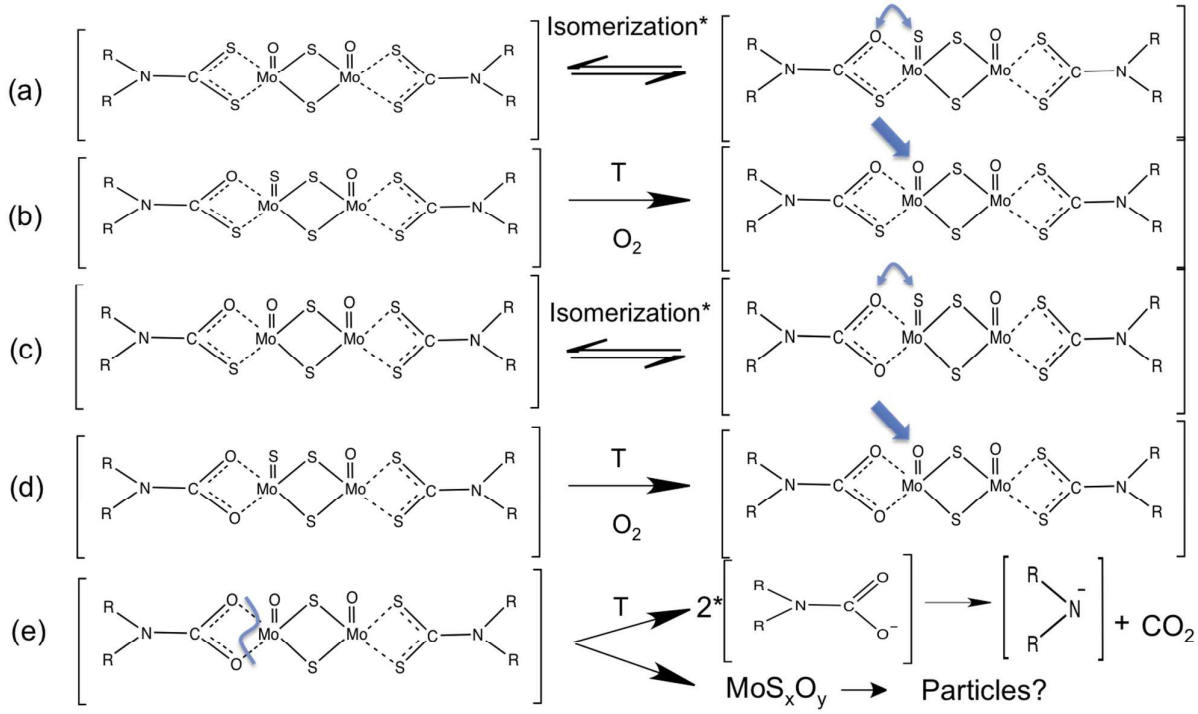

Fig 17. Possible chemical pathway followed by MoDTC molecule during thermo-oxidative degradation

The MoDTC decomposes via a multi-stage reaction pathway:

- firstly an isomerization reaction occurs -a thiolo-diolo rearrangement- characterized by the exchange between the sulfur and oxygen positions (a). This point has been supposed by Onodera et al. after an atomistic and molecular dynamics method [10];

- the sulfur atom double bonded to the molybdenum is then replaced by an oxygen atom (b). This step was deduced by the mass spectroscopy findings. As already explained, it was observed that, when the molecule is subjected to thermo-oxidative degradation, the MoDTC molecular weight decreases of 16 Da. Considering that it corresponds to the difference between sulfur (32) and oxygen (16) molecular weight, it is supposed that during the ageing process there is an oxidation of molybdenum.

- a second isomerization reaction takes place with the sulfur atom changing its position with the oxygen linked to the central molybdenum (c);

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- this sequence, based on the same assumptions, is repeated resulting in the second substitution between an oxygen atom and the sulfur (d);

- the last step is the loss of the R_2NCO_2 group producing the amino group R_2N and carbon dioxide (CO_2);

- the core of MoDTC molecule ($Mo_xS_yO_z$) becomes incorporated into the black particles formed when the additive decomposes, this precipitates out during the degradation process.

The characterization of these particles and their effect on the tribological properties merits further investigations. Furthermore if we consider the behaviour of the HPLC new peak that appears (Figure 7) it seems that following the first degradation period during which a new chemical species is produced, there is then a subsequent depletion of this new reaction product - this is in line with our hypothesis. Also if we assume that this new peak corresponds to the MoDTC molecule with a sulfur atom replaced by an oxygen atom, it is observed that this subsequently converts into another molecule where a further sulfur atom is substituted by an oxygen atom.

V. Conclusions

The results from the complete characterization studies performed here have provided a valuable insight into the changes of the MoDTC friction modifier during thermo-oxidative degradation. Quantification of the additive within the samples has been achieved from a calibration curve using HPLC measurement techniques. In addition with the combined FTIR and MS results a hypothesis for the MoDTC thermal-oxidative degradation chemical pathway has now been proposed.

Our analytical results support the theory that the additive depletion is due to a sulfur-oxygen atom substitution, this then leads to the oxidation and finally the breaking up of the MoDTC molecule itself. Furthermore the oxygen-sulfur replacement within a partially oxidized product molecule appears to take place in an easier way than in fresh MoDTC itself. These findings support our theory that the MoDTC friction performance is primarily due to the presence of partially oxidized MoDTC molecules which are able to lower the friction within the contact.

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