Comparing different analytical techniques to monitor lubricating grease degradation

Authors: Ana Aranzabe[a], Estíbaliz Aranzabe[a], Arrate Marcaide[a], Raquel Ferret[a], Jesús Terradillos[a], Jo Ameye[b]

a: Tekniker, Technological Centre- Avda. Otaola, 20, (20600) Eibar, Spain
b: Fluitec International- Nieuwbrugstraat, 73 B-1830, Brussels, Belgium

Ana obtained a PhD in Chemistry in 1993. After working as teacher in the University in the Inorganic Chemistry Department in the UPV/EHU during two years, in 1995 started working in FUNDACION TEKNIKER a non profit research Centre mainly involved in manufacturing processes. Typical work during these years has been research and development in tribology, mainly lubrication and predictive maintenance. Since 2000 she is the Head of the Tribology Area in the Manufacturing Processes Department. This Area works in friction, wear, lubrication and environment with 20 persons working in research projects, industrial contacts and technical services to industry. Typical research activities mainly involved in are: Determining oxidation stability Methods and remaining useful life in lubricants, predictive maintenance and condition monitoring, lubricants and fuels analysis (implement of biodegradability and toxicity tests to lubricants and greases), chemical processes, biofuels

Mr. Terradillos Azketa
Jesús Terradillos obtained a BSc in Chemistry in 1979 and in 1982 started working at FUNDACION TEKNIKER a non profit research centre mainly involved in manufacturing processes. Typical work during these first years was lubrication and tribology. In 1987 he was in charge of the chemical laboratory, with three years as a member of Wearcheck International group based in predictive maintenance through the analysis of oil. Since 2004 he shares the position of head of the chemical laboratory and the research area of maintenance and surface Chemistry in the Manufacturing Processes Department. His membership in Noria Corporation as franchiser for Spain and Portugal reaffirms his knowledge and expertise with more than 20 years experience in lubricants, with education in industries as one of its main activities. He is a member of the STLE (Society of tribology and lubrication engineers), ELGI (European lubrication greases institute), EUROLAB associations.

1 Summary

During lubricant operation temperature, pressure and load are well known as the main factors enhancing degradation. To monitor this degradation process in lubricating oils, the industry has defined specific test methods involving correct sampling techniques and analytical techniques to provide efficient information on the correct oil change interval. Moreover, modern oil-lubricated systems apply specific oil monitoring procedures as part of condition based maintenance practices to detect root cause failures and prevent equipment damage (1)(2).

Applying these condition monitoring practices on lubricating greases is much more complex as once these greases are put into service, it becomes rather difficult for end-users to perform on-site grease condition monitoring, and define the correct frequency for re-greasing bearings. This explains why industry relies for grease-lubricated systems procedures on time-based intervals (preventive maintenance).In this study, a research using a grease based on mineral oil and lithium soap thickener has been carried out. The grease was oxidised to produce samples at different intervals in order to evaluate different techniques, more specifically: Acid Number (AN), LSV (linear sweep voltammetry - RULER) and FTIR on the grease and its corresponding oil, viscosity, ICP and DSC. Beside the maximum information that the selected analytical techniques should give on the grease condition, the program has also evaluated the minimum quantity of sample, minimum time and the cost of analysis.

During the study, different technologies available on the matter have been compared, which allow the optimization of the frequency of grease changes. Below are shown the different techniques used and the results obtained.

2 Grease degradation detection methods

In order to evaluate the different techniques, a grease sample has been oxidised in a static laboratory test. This oxidation process consisted of subjecting the grease to 125°C temperatures. The sample has been stirred at regular times during the 3 hours oxidation test process.
It's important to select the best techniques to monitor the grease degradation

In the past, various techniques have been used for the detection of oxidation in lubricating oils (1).In the case of greases, we still have a lot to learn. A series of techniques frequently employed in the past have been compared, more precisely:

- A.N. (Acid number) of oil extracted from grease
- IR Spectra of oil extracted from grease (with ether)
- Viscosity at 40°C of oil extra from grease (with ether)
- FTIR of grease
- At the same time, new techniques in this area have been examined:
- DSC (Differential Scanning Calorimetry) test method for grease
- RULER (Linear Sweep Voltammetry) test method on oil extracted from grease

- RULER (Linear Sweep Voltammetry) test method for grease (avoiding solvent extraction phase).

The above test methods were carried out to evaluate their suitability as a laboratory method, as well their ability to detect early grease degradation. Some of techniques have been applied directly to the oil extracted from grease. The extraction of this oil has been carried out by mixture of grease with ether solvent. Then, the mixture has been centrifuged and the solvent has been evaporated from the upper phase.

2.1 Depletion of the antioxidant concentration for oxidised oils

After the extraction of the oil from grease a RULER (Voltammetric) test (3) has been carried out to establish the consumption of antioxidants (expressed as Remaining Useful Life), based on the important role that antioxidants represent in lubricating greases (4, 5).

Figure 1- RULER voltammetric technology

The method for monitoring the amount of antioxidants in greases is based on voltammetric analysis as an electro-analytical method, in which a sample is mixed with an electrolyte and a solvent, and placed in an electrolytic cell (2, 3). The voltammetric test results are based on current, voltage and time relationships at the 3-electrode sensing system with a small, easily polarised microelectrode, and a large non-polarisable reference electrode. In performing a voltammetric analysis, the potential across the electrodes varies linearly with time (from 0 to 1.7 V at a rate of 0.1 V/second), and the resulting current is recorded as a function of the potential. With increased voltage to the sample in the cell, the various dissolved antioxidants oxidize electrochemically resulting in an oxidation reaction that can be used to predict the remaining useful life of the grease or oil type.

In this programme, the voltammetric method was performed with a commercially available voltammograph (RULER©) equipped with a glassy carbon-working electrode, a platinum wire electrode and a platinum wire auxiliary electrode. This instrument can be used both as a laboratory or a field instrument. Table 1 shows the data obtained from oxidation aged oils, subjected to a temperature of 125°C, showing the percentage of antioxidants against their oxidation time

Time (min)	0	15	30	45	60	70	80	90	105	120	135	150	165	300
% Antiox.	100	100	100	95.8	80.1	80.5	77.7	26.9	23.9	1.7	0	0	0	0

Table 1- % of Antioxidants in oil vs. time (minutes) at 125° C oxidation temperature.

Figure 2 below represents the percentage of remaining antioxidants in the oil (extracted with ether from the grease) compared to the respective time at which the grease has been degraded at 125°C temperature.
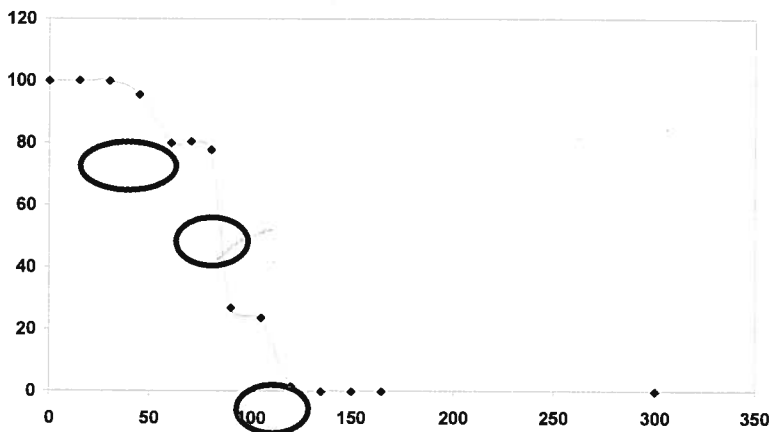

Figure 2- % of Antioxidants on the extracted oil vs. the total oxidation time (min.)

Figure 2 shows how the highest depletion of antioxidants in the oil occurs between 80 and 90 minutes of heating at 125ºC.

2.2 Depletion of antioxidants concentration in grease under conditions of oxidation

A series of RULER tests have been carried out directly on new and oxidized grease samples after different periods of oxidation at 125°C. Once grease samples (max. 250 mg) have been diluted in an acetone/electrolyte mixture, enhancing extraction of the antioxidants (AO[s]) into the solvent phase, oxidation wave peaks have been used to calculate the remaining concentration of antioxidants, as presented in the *Table 2* below. The table shows the obtained data from percentage of grease antioxidants grease against their respective oxidation time (minutes).

Time (min)	0	15	30	45	60	70	80	90	105	120	135	150	165	300
% Antiox.	100	100	100	100	77.6	79.7	72.3	22.2	19.5	0.1	0	0	0	0

Table 2- % Antioxidants in grease vs. time (minutes) at 125° C oxidation temperature.

Figure Below (Figure 3) represents the percentage of remaining antioxidants in the grease (directly performed on the grease sample) compared to the respective time at which the grease has been degraded at 125°C temperature.
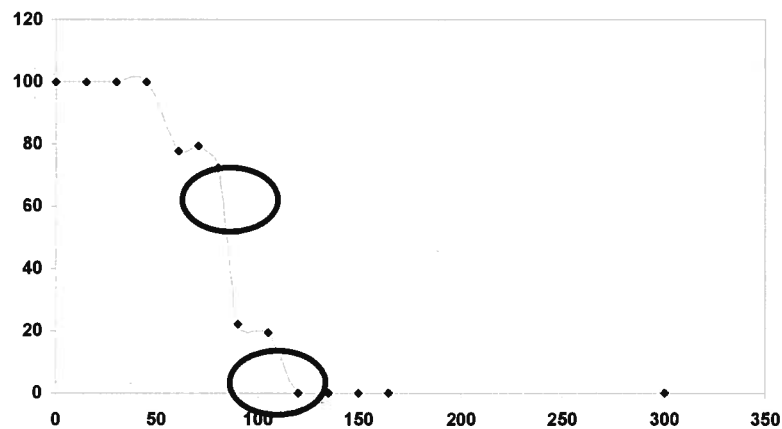

Figure 3-% of Antioxidants for the grease vs. the total oxidation time (min.) –measured directly into the grease.

Figure 3 shows how the highest amount of antioxidants consumption in the grease occurs between 80 and 90 minutes of heating at 125ºC.

2.3 Variation of Acid Number(A.N.) under conditions of oxidation

Both in new lubricants and in-service lubricants, acidic constituents will appear, either in the form of additives or as a result of the oxidation of lubricant. The Acid Number test method *(6)* is a measurement of the quantity of those acidic constituents present into the oil. For this programme, AN measurement has been done following ASTM D 974-04 (a titration which estimates the amount of KOH which is necessary to neutralize the acid compounds of the oil).

Table 3 shows the results obtained from A.N. measurements of the oil extracted both from the new and oxidised grease samples (oxidation test).

Time (min)	0	15	30	45	60	70	80	90	105	120	135	150	165	300
A.N. (mg KOH/g)	2.37	2.44	2.39	2.46	2.64	2.63	2.60	1.22	1.22	0.99	0.83	0.78	1.02	1.75

Table 3- A.N. of oxidised oils in function of the total oxidation time (min).

A drop in the A.N. can be observed between 80 and 90 minutes of degradation. This decrease is due to the loss of additives in the grease. Between 165 and 300 minutes an increase in A.N. can be seen due

to the onset of the degradation of the oil. Figure below represents the results obtained in A.N. measurements over different periods of time of oxidation.
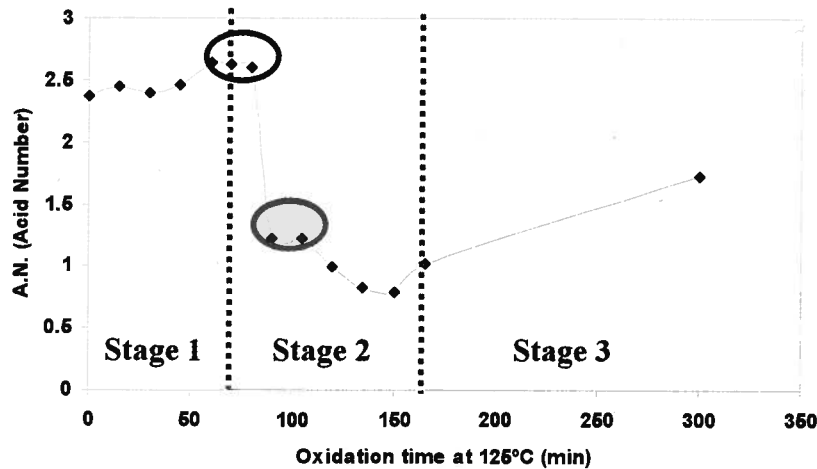

Figure 4- A.N. (Acid number) vs. the total oxidation time (min.) of the grease.

From this AN graph we can distinct 3 stages as shown in Figure 4.

- **Stage 1. % of Antioxidants remains constant (from 0 to 80 minutes of degradation)**
The condition of the oil hardly varies during the first minutes of oxidation, as the remaining concentration of antioxidants will protect the lubricant against oxidation.
- **Stage 2. Depletion of antioxidants (from 80 to 150 minutes of degradation)**
Due to the antioxidant concentration, the new oil has shown such a high AN (2.37 mg KOH/g). When the loss of additives is occurring, the AN starts to decrease, and as it is shown in the graph the greater decrease in AN of the oil occurs between 80 and 90 minutes at this temperature. This is in good correlation with the RULER test data for antioxidant detection.
- **Stage 3. The degradation of the base oil (> 150 minutes)**
After 150 minutes of total oxidation time, when the antioxidant additives have been exhausted, the base oil starts being oxidised producing a series of oxidation compounds which results in the increase of the acidity. This base oil degradation will logically result in an increase of the AN on the oil extracted from the grease.

2.4 Variation in the IR spectra for the oxidised oil samples.
The IR Spectroscopy is a well known technique for analysing the chemical properties of the oil such as oxidation products or antioxidant additives.
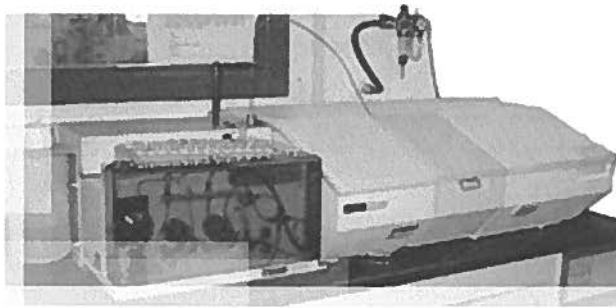
Figure 5- FT/IR Perkin Elmer Spectrum BX-I

To perform grease samples spectroscopic test by IR, the oil was extracted from the new grease as well as from oxidation test aged grease samples (with ether solvent). Subsequently an IR test has been carried out for each oil sample, as shown in the IR spectra of the oils (Figure 6).
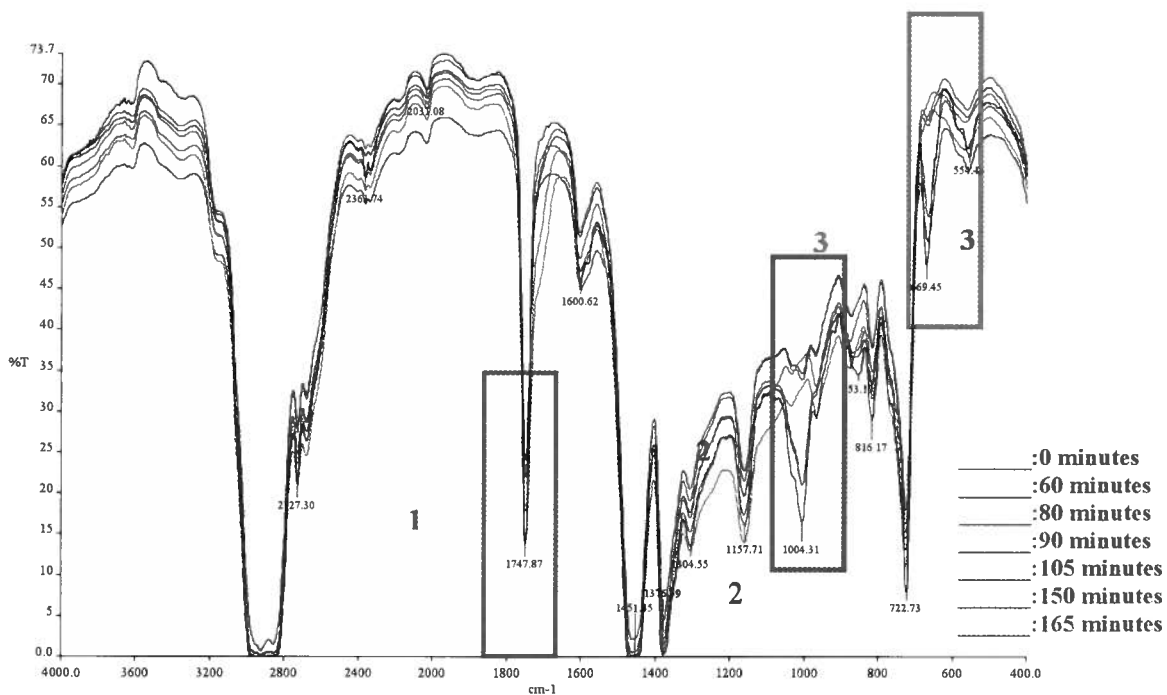

Figure 6- IR spectra of the extracted oils.

In Figure 6 changes of area in the spectra of the oil can be seen, and applying the IR-method the following IR Spectra areas will be selected:

- **Zone 1- 1780 cm^{-1}-1700 cm^{-1}:** This zone corresponds to the EP additive which, in principle, should not be affected by the laboratory oxidation test. Furthermore, oxidised compounds can also be observed.

- **Zone 2- 960 cm^{-1}-1020 cm^{-1}:** This zone corresponds to the ZDDP antioxidant additive, which we can expect to be affected under oxidation.

- **Zone 3- 650 cm^{-1}-690 cm^{-1}:** This zone corresponds also to the ZDDP antioxidant additive.

2.4.1   Zone:1780 cm^{-1} - 1700 cm^{-1}

_____ :0 minutes
_____ :60 minutes
_____ :80 minutes
_____ :90 minutes
_____ :105 minutes
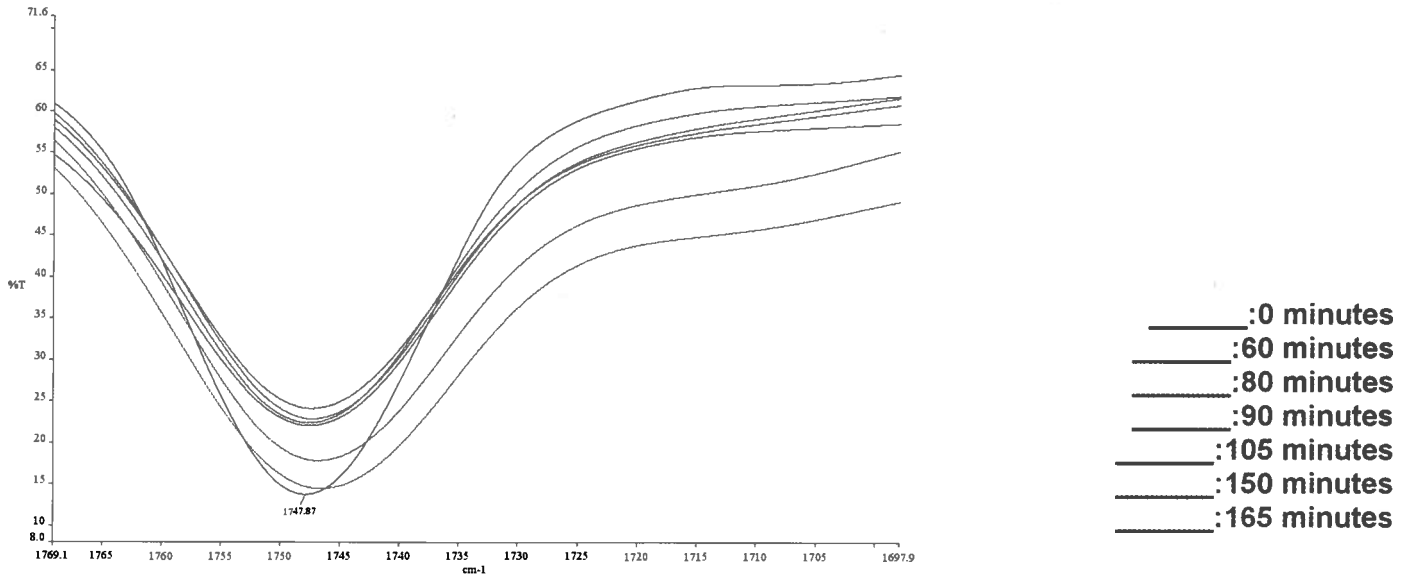_____ :150 minutes
_____ :165 minutes

Figure 7- Zone 1780 cm^{-1} - 1700 cm^{-1}

As shown in Figure 7, the band becomes wider to the right over a period of time. This effect won't be seen in every case due to an overlap with the additive and the other oxidised compounds.
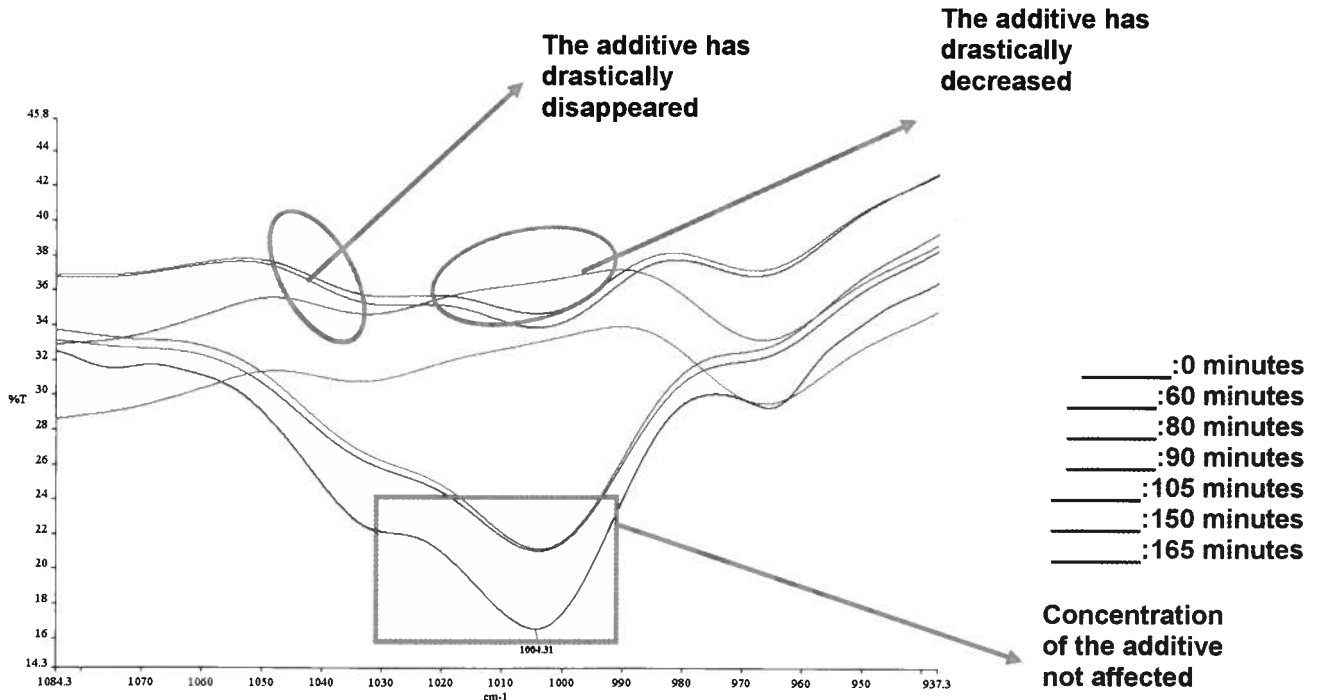
2.4.2   Zone:960 cm^{-1} - 1020 cm^{-1}

The additive has drastically disappeared

The additive has drastically decreased

_____ :0 minutes
_____ :60 minutes
_____ :80 minutes
_____ :90 minutes
_____ :105 minutes
_____ :150 minutes
_____ :165 minutes

Concentration of the additive not affected

Figure 8- Zone 960 cm^{-1} - 1020 cm^{-1}

The band corresponding to the P-O-C bond of the additive is disappearing. In fact, the additive decreases considerably between 80 and 90 minutes of oxidation. The additive disappears completely between 105 and 150 minutes of oxidation.

2.4.3 Zone: 650 cm⁻¹ - 690 cm⁻¹

The additive has drastically disappeared

The additive has decreased drastically

_____: 0 minutes
_____: 60 minutes
_____: 80 minutes
_____: 90 minutes
_____: 105 minutes
_____: 150 minutes
_____: 165 minutes
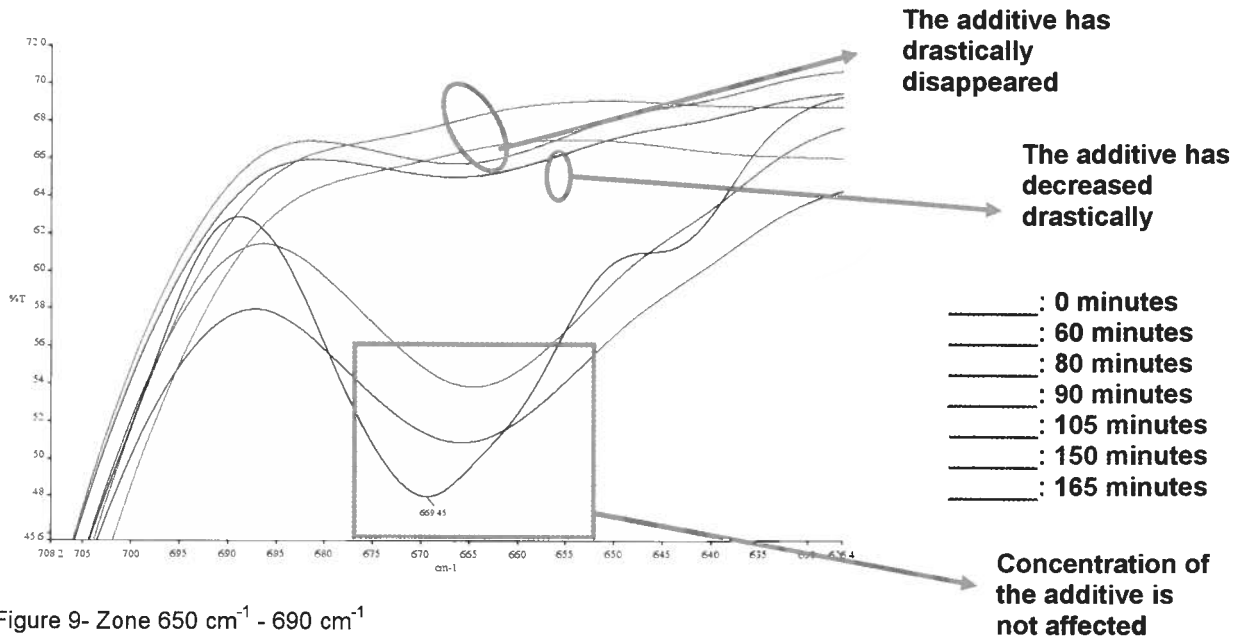
Concentration of the additive is not affected

Figure 9- Zone 650 cm⁻¹ - 690 cm⁻¹

The band corresponding to P=S bond of the additive (ZDDP) is disappearing. The additive decreases drastically between 80 and 90 minutes of oxidation and it disappears completely between 105 and 150 minutes of oxidation. *Table 4* shows the band areas for the corresponding ZDDP antioxidant.

	BAND AREA 688 cm⁻¹-621 cm⁻¹	BAND AREA 1080 cm⁻¹-973 cm⁻¹
0	16.5245	65.0606
60	16.3429	64.1869
80	14.74	63.4799
90	12.2826	59.3212
105	11.9999	58.9865
150	11.2013	56.7865
165	11.2265	56.8097

Table 4- Band areas for corresponding ZDDP additives

In order to calculate the % of remaining antioxidants in the different oil samples, we have established the following conditions:

• The % of additives in the oil is 100 at 0 minutes.
• The % of additives in the oil is zero at 165 minutes.

These conditions are based on RULER and A.N. test results.

Table 5 shows the % of the additive in the corresponding band areas for the ZDDP additive:

	% of Additive Band Area 688 cm⁻¹-621 cm⁻¹	% of Additive Band Area 1080 cm⁻¹-973 cm⁻¹
0	100	100
60	96.59	89.44
80	66.59	80.89
90	20.31	30.6
105	15.00	26.54
150	0	0
165	0	0

Table 5- % of Remaining ZDDP vs. Band Areas (cm⁻¹).

Table 5 shows that the largest reduction of antioxidants concentration for the IR spectra bands, occurs between 80 and 90 minutes of grease degradation. These results correlate well with the results obtained from RULER test (on oil extracted from grease as well directly on the grease) and by AN test on the oil samples.

2.5 Variation in the Zn and P content by ICP

The Atomic Emission Spectroscopy is a useful technique to determine quickly and accurately the concentrations (ppm) of the different elements in greases which can be present as additives, wear particles or other contaminants (per ASTM D 5185 (7) standard test method). Due to the ability of ICP test method to detect elements as Zinc (Zn) and phosphor (P), it can be a good method to detect the depletion of the antioxidants in the grease by means the antioxidants contents Zn and P.
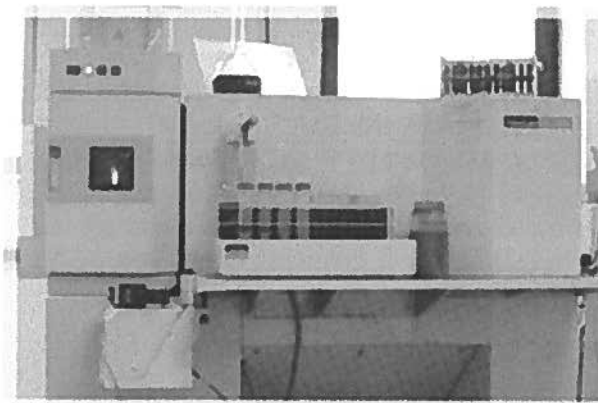

Figure 10- EOS-ICP -Perkin Elmer Optima 3300 RL

If the antioxidant additive of the grease cannot be detected by ICP, this technique will be underestimated. The utility of this technique will be evaluated by measuring the Zn and P content of the antioxidants for different types of greases. *Table 6* shows the results of the Zn and P concentration (ppm) for the grease samples after different times of oxidation (min).

Degradation time (min) at 125°C	[Zn] (ppm)	[P] (ppm)	% Zn	% P
0	1855	1232	100	100
15	1803	1211	97.20	98.29
30	1725	1179	92.99	95.70
45	1673	1213	90.19	98.46
60	1589	1117	85.66	90.66
70	1662	1180	89.59	95.78
80	1550	1149	83.56	93.26
90	1083	972	58.38	78.90
105	975	876	52.56	71.10
120	779	750	41.99	60.88
135	799	769	43.07	62.42
150	769	796	41.45	64.61
165	789	769	42.53	62.42
300	779	759	41.99	61.61

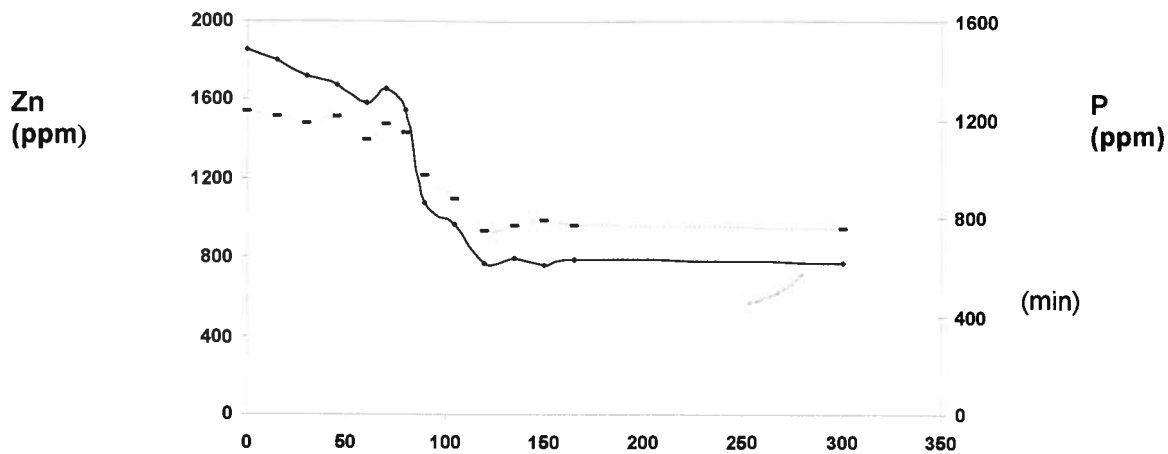Table 6- Zn and P (ppm) concentration vs. the grease oxidation time (min.)

Figure 11 shows a clear decrease in the Zn and P content over time of oxidation. The largest depletion occurs between 80 and 90 minutes (as shown by the RULER, the AN and the FTIR test methods). After 120 minutes, the Zn and P concentration detected by the ICP does not decrease any further. Therefore, the conclusion could be that the additive has to be considered totally depleted (although part of these elements remain in the grease after the dissociation). In order to calculate the % of antioxidants remaining in different oils, we have to establish the following conditions:

- The % of additives in the oil is 100 at 0 minutes.
- The % of additives in the oil is zero at 120 minutes.

The results are summarised in Table 7 showing the % of the antioxidant additives vs. their respective oxidation time:

Time of oxidation (minutes)	% of Zn content	% of P content	AVERAGE (% of the additive)
0	100	100	100
15	95.16	95.64	95.4
30	87.92	89.00	88.46
45	83.08	96.05	89.56
60	75.28	76.14	75.71
70	82.00	89.11	85.55
80	71.65	82.78	77.21
90	28.25	46.05	37.15
105	18.21	26.14	22.17
120	0	0	0
135	0	0	0
150	0	0	0
165	0	0	0
300	0	0	0

Table 7- % of the antioxidants in the grease vs. the oxidation time (min.)

2.6 Variation of the viscosity at 40°C

The viscosity remains the most important property of the oil as part of the oil condition monitoring. Viscosity measurements have been performed on the extracted oil (per ASTM D 445 (8)). In general, the variation of oil viscosity can be caused by:

- The increase of viscosity results from the oxidation and/or polymerization of the oil, evaporation of the most light fractions even water presence or insoluble oxides formation.
- The decrease of viscosity may be due to thermal cracking of the molecules of the lubricant, or shear stress from the viscosity modifiers
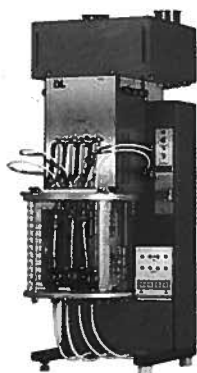
Figure 12- Viscosimeter Houillon V066/230

Time	0	15	30	45	60	70	80	90	105	120	135	150	165	300
Visco 40°C	139.45	137.45	135.89	135.90	133.63	134.44	134.46	133.66	133.90	133.92	133.95	133.92	134.59	140.62

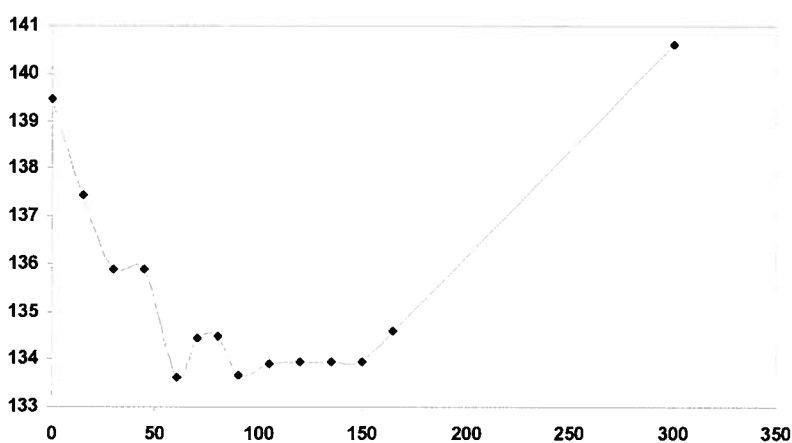Table 8- Variation of viscosity at 40°C vs. the oxidation time (min.)

Figure 13- Variation of viscosity at 40°C over time of oxidation

Figure 13 shows the results of the viscosity at 40°C over different times of oxidation. The evolution of the viscosity at 40°C is not clear. At the beginning, it shows a slight decrease and after that, it begins to increase slightly but in neither case is the change significant. For this reason, no conclusion is drawn about the analysis of viscosity at 40°C under different conditions of oxidation. The viscosity would not be affected by the degradation of grease (at least in the first stages of its degradation).

2.7 DSC Variation

The DSC is a thermal analysis laboratory test that measures the heat flow associated with certain physical and chemical changes in a lubricant. By applying a constant temperature, the degradation of lubricant occurs in a precise time (Onset Time) with the resulting emission of heat (exothermic process). A sufficiently high temperature has been selected to produce a well-defined signal (exothermic process) of the degradation for the new grease and their corresponding oxidized samples. The sample is placed in an oven heated to a set temperature, in this case at 180°C. Oxygen is then passed over the 2 cells, and when the antioxidant in the sample can no longer afford protection, oxidation of the lubricant takes place and is detected by a temperature rise in the cell containing the sample. Although this technique can give important data about the thermal properties of lubricants over a wide range of temperatures, the tests conducted in this program focus on the variation in the times from the beginning of the degradation of the new grease and its corresponding oxidised forms at a given temperature (180°C). The tests have

been carried out using the same variations per ASTM D 5483 (9) and with following test conditions chosen:

- o 50.0°C - 180°C at 10°C/min and 180°C for 120 minutes.
- o 3.8 - 4.2 mg of sample.
- o Copper crucibles without pin.
- o 50 ml/min of oxygen.

Table 9 shows the results for new grease and their corresponding used samples with DSC.
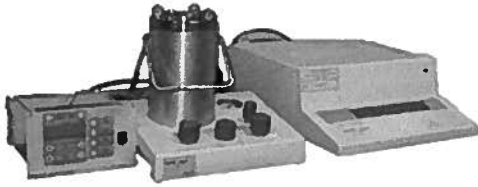

Figure 14- Mettler DSC27HP

Time of oxidation (minutes)	DSC (onset time, minutes)
0	33.11
45	28.24
60	26.57
70	26.27
80	26.06
90	23.79
165	23.28

Table 9- Results of the DSC analysis results for oxidised grease at 125°C

A proportional decrease in the onset time can be observed in the different oxidized samples compared with new grease at a given temperature, which means that the most highly oxidized samples take a short time to begin degradation at 180°C. – see Figure 15 showing a typical thermogram obtained by overlapping different samples.
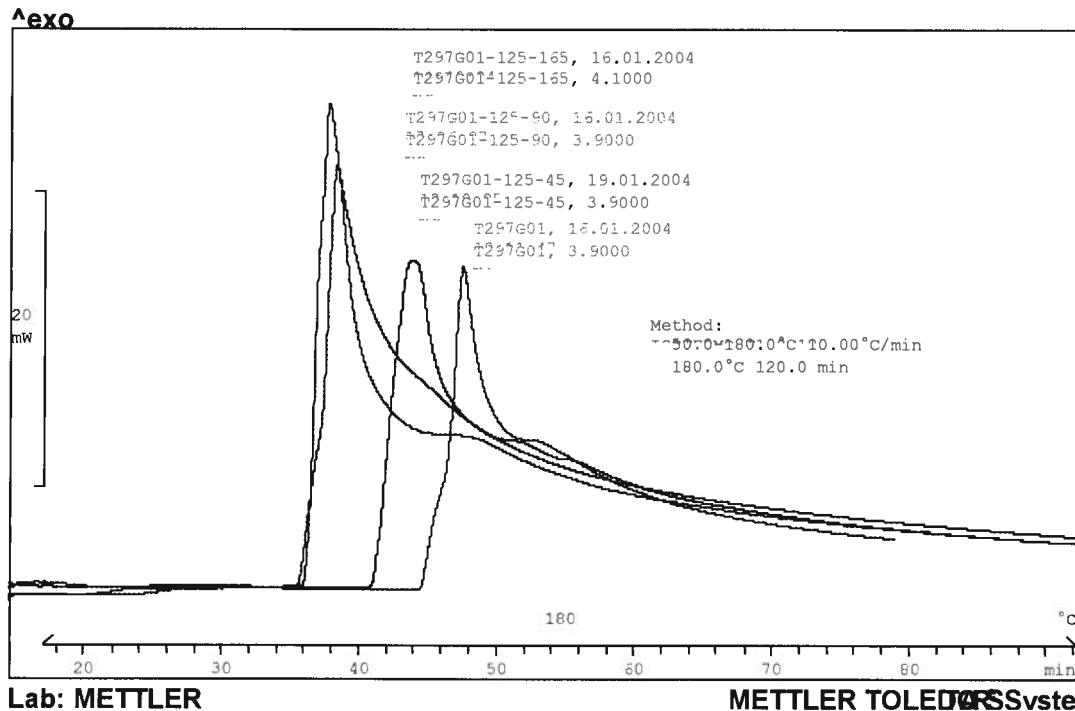

Lab: METTLER
METTLER TOLEDO RSSystem

Figure 15- DSC Thermograms

_____: T297G01
_____: T297G01-45
_____: T297G01-90
_____: T297G01-165

It can be clearly seen from all the results which are the corresponding peaks to the heat emission from which the onset time has been calculated. It can also be seen how the on-set time at the test temperature is irreversibly correlating with the degree of oxidation of the oil sample.

2.8 Variation in the IR spectra for the grease

The FTIR analysis test has been performed directly on grease samples. Grease spectra by FTIR can supply information about the condition of grease, but it is not quantifiable. This can be explained taking into account that in the FTIR test of a grease there are other factors that may interfere in comparison to the FTIR test made for oil extracted from grease.
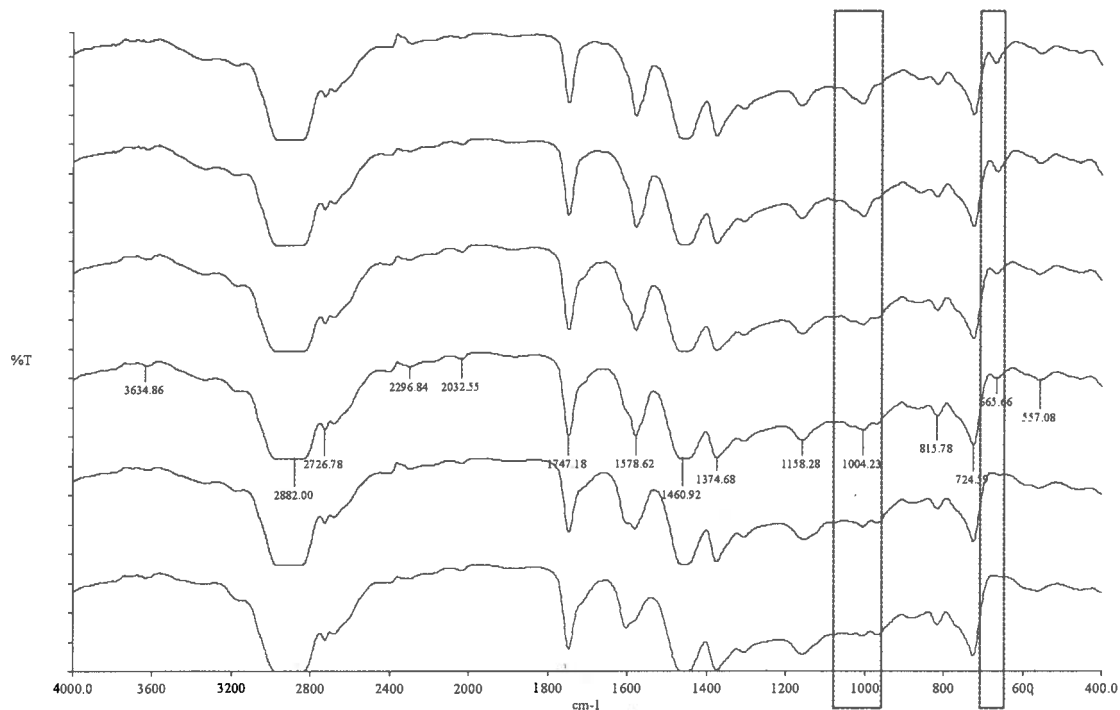

Figure 16- IR spectra of grease samples

From the FTIR spectra above, it can be clearly seen how additives concentration is decreasing, but this decrease cannot be quantified because is difficult to reproduce the same thickness of grease in the cells of the FTIR.

3 Correlation between the different grease test methods: IR Spectra on the oil vs. RULER – A.N. (Acid Number)

3.1 RULER Test results (% remaining antioxidants)

RULER test results have been achieved both for grease extracted oil samples and directly on the grease. It can be concluded that the depletion of the antioxidants is detected after an interval of 80 to 90 minutes, suggesting that the base oil is starting to degrade. Figure 17 represents the variation in the antioxidants (on the grease and on the oil) compared with the time of oxidation.
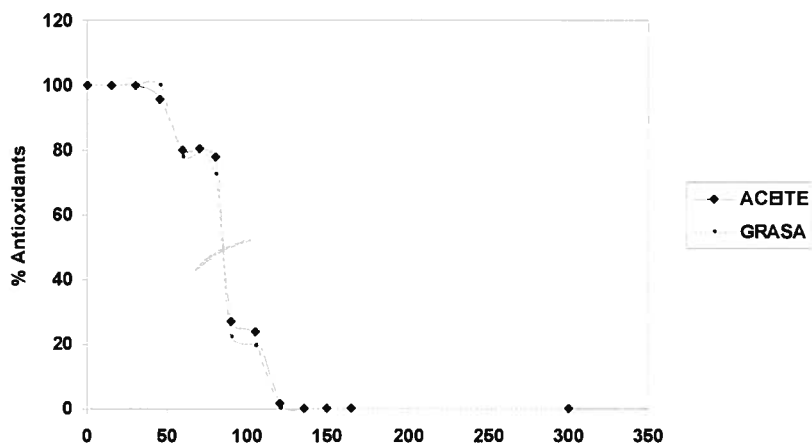

Figure 17- Variation of antioxidants concentration vs. time of oxidation.

3.2 A.N. (Acid Number)

The degree of acidity on the oils extracted from grease samples have been compared with the results obtained by RULER test method (*Figure 18*). The decrease of the AN and the % of antioxidants in the oil are occurring clearly at the same time (between 80 and 90 minutes).
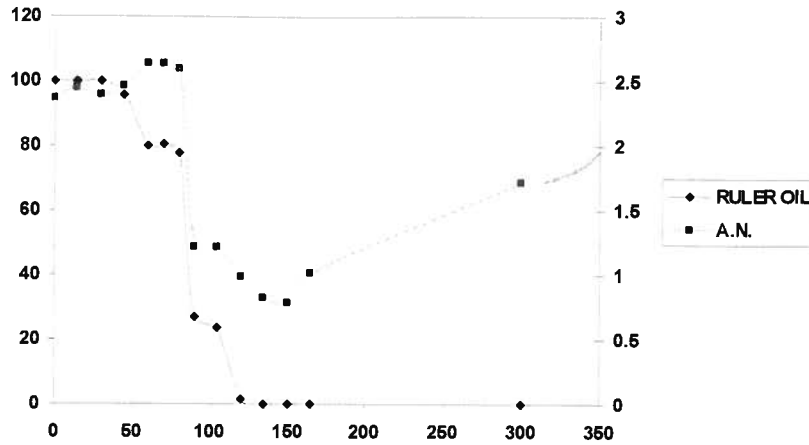
Figure 18- % of Antioxidants, A.N. vs time of oxidation

3.3 IR Spectra on the oil extracted from the grease

Also the IR spectra clearly show that there is a significant decrease of the additives between 80 and 90 minutes. The graph below shows the IR band 680 cm^{-1} - 620 cm^{-1} (which corresponds with the ZDDP additive) where a perfect correlation with the antioxidant concentration with the RULER test method can be seen.
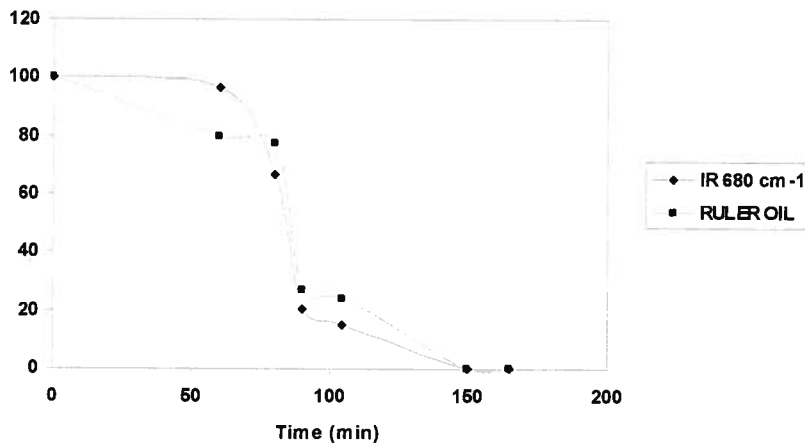
Figure 19- % of Antioxidants (by RULER and IR (680-620) vs. time of oxidation

The following graph shows how the IR band from 1080 cm^{-1} to 970 cm^{-1} (which corresponds at ZDDP additive) correlates perfectly with RULER test.
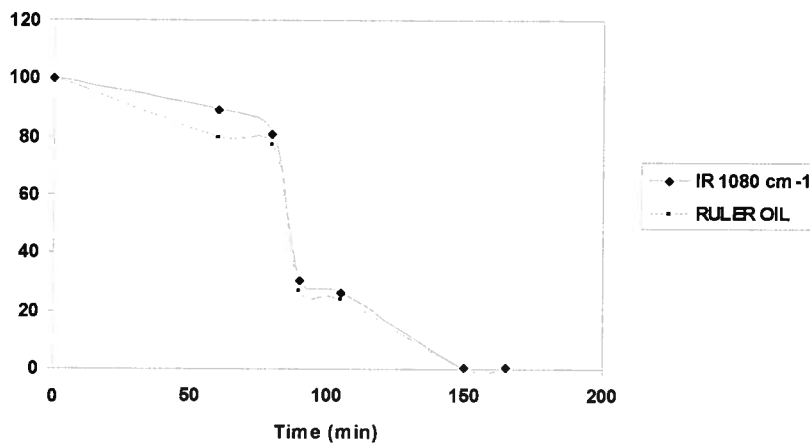
Figure 20- % of antioxidants (by RULER), IR (1080-970) vs. time of oxidation

3.4 ICP on the grease

A clear decrease in the Zn and P content can be observed during the oxidation process. The biggest drop is detected between 80 and 90 minutes. After 120 minutes the Zn and P concentration does not decrease any further, which mean that the additive can be considered totally depleted.
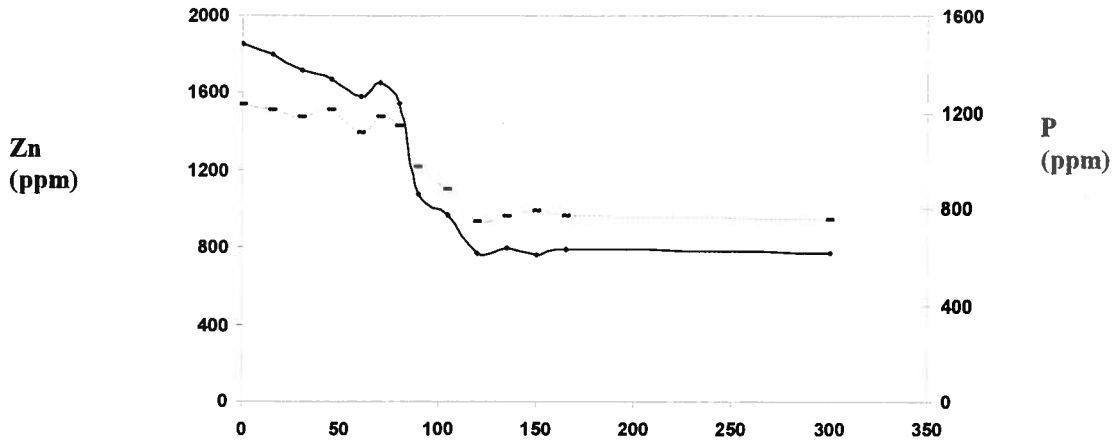

Figure 21- P and Zn concentration (ppm) vs. time of oxidation

From all the test results obtained, it can conclude that the following analytical test methods are all correlating:

- RULER test (both for grease and for oil extracted from grease)
- Acid Number (AN),
- IR Spectroscopy
- the measurement of the Zn and P content by ICP

Considering that these methods detect the consumption of the antioxidant additives in oxidized greases, they can be applied as valid test methods for detecting oxidation in greases. The decrease in the AN is caused by the loss of additives (which can be measured by IR Spectroscopy, by RULER and by ICP): the initial acidity of the oil is due to presence of additives mentioned above. *Figure 22* below shows the good correlation between these 4 techniques.
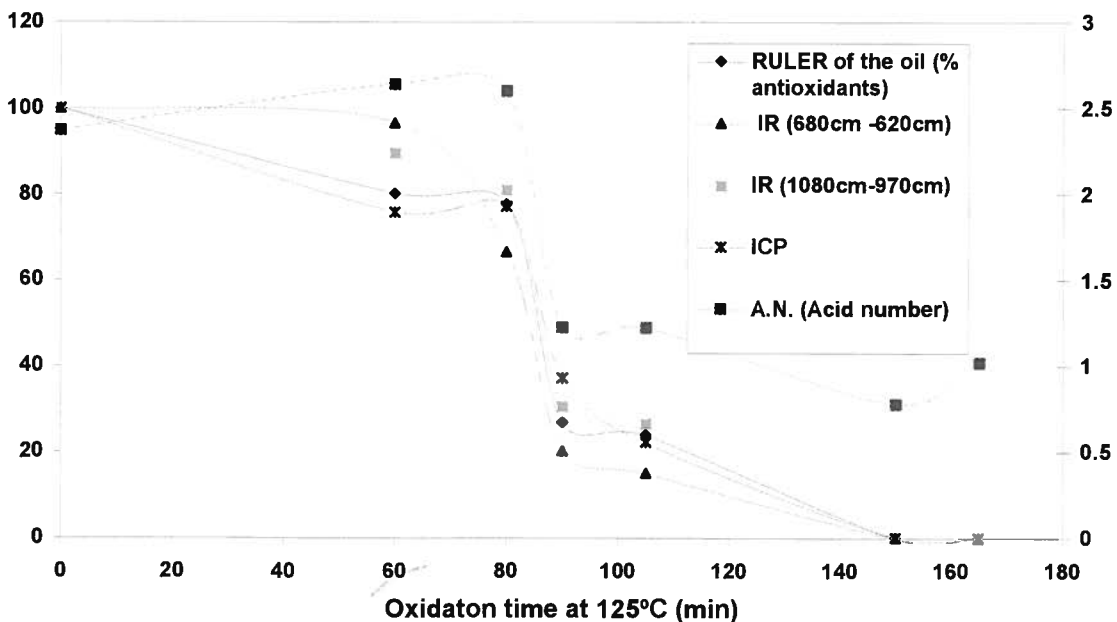

Figure 22- % of Antioxidants (by RULER for the grease, by RULER for the oil, by IR (1080-970), IR (682-620) and ICP) and A.N. (acid number) vs. time of oxidation.

The graph shows (Figure 22) the point at which the additives become depleted. Detecting this critical point, users would have the possibility to change the grease before it starts oxidizing severely.

3.5 Viscosity @ 40°C vs. A.N. (Acid number)

Figure 23 shows the relation between viscosity at 40°C and the A.N. during the oxidation period.
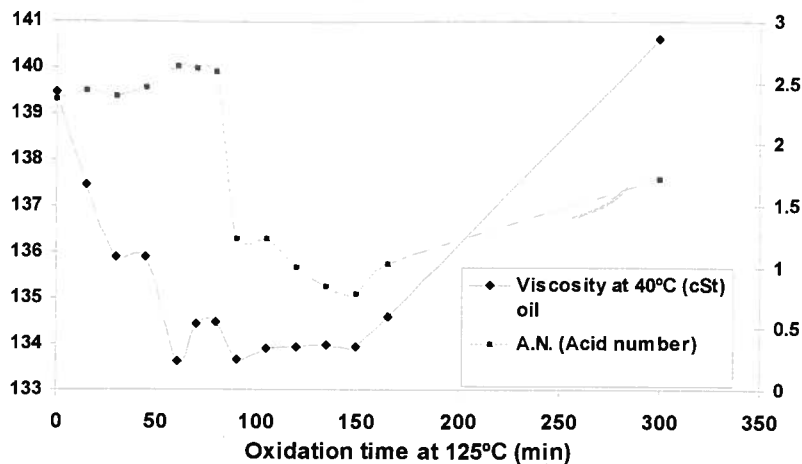

Figure 23- Viscosity at 40°C and A.N. vs. time of oxidation

Certain correlations can be observed between viscosity at 40°C and the A.N. (Acid Number) but these are not enough clear. The test method for viscosity measurement (at 40°C), do not detect the consumption of additives. That is the reason why it cannot be used as an early indication of oxidation. The changes in the viscosity (at 40°C) occur mostly when the oxidation of grease is clearly advanced, so it would not be suitable for detection of degradation before this stage.

3.6 DSC vs. RULER on oil

The DSC test method is a method to calculate the useful life of the lubricant and would be a valid technique to monitor the degree of grease degradation. However, an in-depth study of the behaviour of grease at different test temperatures is required enabling to correlate the different onset times obtained from other analytical techniques the results other analytical techniques.
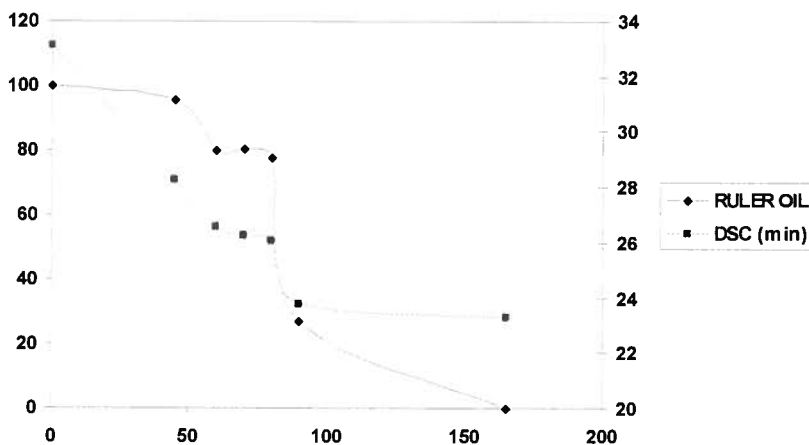

Figure 24- % of Antioxidants and DSC vs time of oxidation

4 Summary of the test results obtained by different grease test methods

	VISCOSITY		FTIR		RULER		A.N.	ICP			DSC
Oxidation time at 125°C (min)	Viscosity at 40°C of the oil (cSt)	Viscosity at 100°C of the oil (cSt)	% antioxidants IR @ 688 cm⁻¹ - 621 cm⁻¹	% antioxidants IR @ 1080 cm⁻¹ - 973 cm⁻¹	RULER (% antioxidants) for the grease	RULER (% antioxidants) for the oil	A.N. (Acid number) for the oil	% Antioxidants by ICP (Zn & P)	% Zn from the initial concentr.	% of P from the initial concentr.	Time (min)
0	139.45	14.05	100	100	100	100	2.37	100	100	100	33.11
15	137.45	13.96	-	-	100	100	2.44	95.4	97.20	98.29	-
30	135.89	13.94	-	-	100	100	2.39	88.46	92.99	95.70	-
45	135.90	13.85	-	-	100	95.8	2.46	89.56	90.19	98.46	28.24
60	133.63	13.71	96.59	89.44	77.6	80.1	2.64	75.71	85.66	90.66	26.57
70	134.44	13.69	-	-	79.7	80.5	2.63	85.55	89.59	95.78	26.27
80	134.46	13.86	66.59	80.89	72.3	77.7	2.60	77.21	83.56	93.26	26.06
90	133.66	13.65	20.31	30.6	22.2	26.9	1.22	37.15	58.38	78.90	23.79
105	133.90	13.64	15.00	26.54	19.5	23.9	1.22	22.17	52.56	71.10	-
120	133.92	13.66	-	-	0.1	1.7	0.99	0	41.99	60.88	-
135	133.95	13.72	-	-	0	0	0.83	0	43.07	62.42	-
150	133.92	13.58	0	0	0	0	0.78	0	41.45	64.61	-
165	134.59	13.73	0	0	0	0	1.02	0	42.53	62.42	23.28
300	140.62	14.06	-	-	0	0	1.72	0	41.99	61.61	-

Table 10- Summary of test results

5 Conclusions

From this research program performed on grease samples, the following conclusions can be made:

5.1

The most suitable techniques to identify the degradation at an early stage by means the monitoring of early consumption of antioxidant additives, are:

- **Ruler**

By applying the RULER test method, operators will monitor the Remaining Useful Grease life, both for field as laboratory application by giving a test result as the percentage of remaining antioxidants in the grease. This test method can be performed directly on the grease or by extracting the oil from the grease. This last option is interesting as it avoid the more expensive, time consuming and complicated procedure of extracting oil from the grease.

- **IR Spectra for the oil**

By measuring the IR bands which correspond to the antioxidants additives present in the oil, it is possible to obtain the percentage of antioxidants remaining in grease. This method has various <u>disadvantages</u>:

- o Antioxidant additive type ZDDP can be quantified using the IR Spectra. However, it would be necessary to study the viability of this technique in the case of ashless types of antioxidants, like phenol and amine type.
- o In order to quantify the % of ZDDP antioxidant additives in the grease, a laboratory test must be performed first in order to oxidise the grease completely and consequently to be able to measure the area of the band at which the % of antioxidants is zero.

- **ICP**

By measuring the content of the elements which make up the antioxidant additive, it is possible to obtain the % of antioxidants which remain in the grease. This method has several <u>disadvantages</u>:

- o It is not possible to quantify all types of antioxidants by means of ICP.
- o In order to calculate the % of antioxidants remaining in the grease a laboratory test must be performed first involving the complete oxidation of the grease to be able to measure the band at which the % of antioxidants is zero.

Techniques such as A.N. (Acid Number) or Viscosity are more useful for detecting the degradation once it has begun. By means of these tests it is possible to quantify which is the stage of oxidation that lubricant has reached. It is not possible quantify oxidation values by means of RULER or ICP.

5.2

It has been found that IR Spectroscopy test method is quite useful both in the detection of the decrease of antioxidant additives (early indication of oxidation) and for calculating the degree of oxidation (once it has begun). The band areas to be observed will be different depending on what is required:

- o To observe a decrease in the antioxidant additives, the corresponding bands will be examined (in the case that the antioxidants can be detected and measured by FTIR.
- o To quantify oxidation in a lubricant, the bands to be observed are those corresponding to the oxidation products (carbonyl functional groups).

5.3

For DSC test method, as mentioned in this paper, a wider study would have to be carried out in order to calculate the useful life of lubricating greases.

5.4

The results from ICP test method has shown that the antioxidant additive is depleted when approximately 50% of the compounds which form the ZDDP additives (Zn and P) are still present in the sample (*Table 10*).

5 Reference list

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