

TESTING THERMAL STABILITIES OF BASE OILS AND THEIR ADDITIVES VIA HIGH-TEMPERATURE INFRARED SPECTROSCOPY

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The thermal stabilities of base oils and their additives could be examined by employing an infrared spectroscopic technique. As the heat temperature was increased, changes in absorption were recorded at different wavelengths characteristic of the chemical groups. These changes were observed to occur slowly at first, but then turn to become more marked at specific temperatures. The magnitudes of these changes and temperatures were taken as indications of the thermal stabilities of the samples. The thermal stability was found to decrease in the following sequence: aromatics > naphthenes > hetero compounds > substituted aromatic rings > paraffins.

Infrared (IR) spectroscopy has been used extensively during the past two decades to evaluate the performance of lubricating oils during their service periods [1-2]. The chemical changes that occur in these oils inside engines have been studied [3-4], and the activities of incorporated additives have been assessed [5-6]. The results of these studies have helped greatly to extend the time between oil drainage periods.

IR spectroscopy has also been combined with other measurement techniques, such as membrane filtration and column chromatography [6, 7]. Attempts have also been made to evaluate the thermal behaviour of base oils by IR spectroscopic means [8-9].

Lewis and Edsrom [10] used DTA in conjunction with gas chromatography and IR spectrophotometry to study the thermal behaviour of polynuclear aromatics.

The present paper deals with the development of an IR spectroscopic procedure capable of evaluating the thermal stabilities of base oils, with and without additives.

Experimental

Three different base oils (samples 1, 2 and 3), with the analytical data given in Table 1, were used through the study. Oils 1 and 2 are neutral base oils with some differences in their physical properties (e.g. specific gravity, molecular weight, flash point, viscosity, etc.) and chemical structure (saturates, aromatics, type of aromatics, etc.). Oil 3 is a typical bright-stock oil with a relatively high viscosity. These oils were chosen in order to investigate the sensitivity of the developed IR spectroscopic technique to such different oils.

The IR spectra of the base oil samples were recorded on a differential double-beam Perkin-Elmer spectrophotometer. The sample cell can be heated to any specific measurement temperature (from -190° to $+250^{\circ}$) by means of an electric device provided with a variable-temperature controller.

As thermal analysis can be affected by the measurement conditions on the IR spectrophotometer, it was essential to specify first some of the measurement variables (e.g. type of cell windows, cell prethermal treatment, time between two

Table 1 Analysis figures for base oils

Analysis figures	Base oils		
	1	2	3
Specific gravity (a : $15/4^{\circ}\text{C}$, (IP 160/68)	0.8815	0.8855	0.8985
Colour, (IP 1966)	2	2.5	5
Flash point—closed ($^{\circ}\text{F}$), (IP 34/67)	470	410	520
Pour point ($^{\circ}\text{C}$), (IP 15/67)	-6	-6	-9
Conradson Carbon (% wt), (IP 13/66)	0.011	0.008	0.4
Ash (% wt), (IP 481)	nil	nil	0.003
Total acid number mg KOH/g sample, (IP 177/64)	0.03	0.03	0.02
Viscosity at 40°C (cSt), (IP 71/73)	103.6	55.6	520.9
Viscosity at 100°C (cSt), (IP 71/73)	11.34	7.43	32.6
Viscosity index (IP 226/68)	95	93	94
Aniline point ($^{\circ}\text{C}$) (IP 2/61)	117	105	125
Mean Molecular weight ⁽¹²⁾ <i>n-d-m</i> method. ⁽¹³⁾	510	450	760
C_N % mole	25.9	29.0	22.2
C_P % mole	68.5	63.8	70.7
C_A % mole	5.6	7.2	7.1
Hydrocarbon classes % wt ⁽¹⁴⁾ saturates	67	66.1	35.0
Monocyclic Aromatics	33.0	15.3	60.0
Dicyclic Aromatics	—	15.8	—
Polycyclic and Resin	—	2.8	5.0
Total sulphur % wt ⁽¹⁵⁾	0.28	0.40	0.71
Total Nitrogen % wt ⁽¹⁶⁾	0.0123	0.0244	0.0103

successive measurements, chart speed, scanning time, magnitude of spectrum expansion, etc.).

Another set of variables was also found to affect the accuracy of the results, including the layer thickness, the sample density and the ease with which gaseous effluents were released from the cell. After all these variables had been specified as mentioned in Table 2, the following procedure was applied:

1. The base oil sample was injected at room temperature into both the sample cell and the reference cell.
2. The spectrophotometer scanned the full IR spectrum range and the baseline was fixed at 40% (T).
3. The sample cell temperature was elevated from room temperature directly to 80°. This temperature was found to be inert towards the expected changes in IR absorption.
4. The temperature was kept constant at 80° while the IR spectrum was running for the normal scanning time (6 min).
5. The temperature was then raised in a stepwise manner to 90°, and full IR spectrum measurement was repeated every 10°.

Table 2 Working conditions for heatable cell infrared spectroscopic technique

Measurement variables	Working conditions
Material of cell windows	KBr (after thermal treatment)
Cell thickness, mm	0.1
Scanning time, min.	6
Interval time (between two successive measurements) min.	5
Heating range	from ambient up to 250°

It was found necessary before beginning to perform prethermal treatment of the cells. This was carried out by putting the new empty cells in an oven at 100° for one hour, and then leaving them to cool to room temperature in a desiccator. Heating and cooling cycles were repeated in the same manner at 150°, 200° and 300°. Such treatment was found satisfactory and prevented fractures of the cell windows during test measurements.

At the beginning of the test, the sample cell was heated directly to 80°, the temperature was then kept constant for exactly 5 minutes, and the full IR spectrum was recorded.

At some specific wavelengths, the amplitude of the band absorption was high enough to exceed the chart. The temperatures at these points were recorded and they were termed break-points i.e. points where the slope of the absorbance vs.

temperature curve changes. The rates of change in band absorption ($A \approx \log I/I$) at these wavelengths were recorded against measurement temperature, and until the occurrence of high-amplitude absorption, i.e. at the sensitive temperatures.

Results and discussion

The evaluation of the thermal behaviour of the base oils by the procedure adopted in this paper is dependent on the applied experimental conditions (Table 2). Differences can be attributed to the following measurement variables: type of

Table 3 – Log I_0/I at wave number 720 cm^{-1} with different cell material

Cell type	AgCl cells		KBr cells	
	1st measurements	3rd measurements	1st measurements	3rd measurements
Test temp. °C				
80	0.119	0.112	0.112	0.12
90	0.185	0.161	0.193	0.191
100	0.245	0.230	0.251	0.251
110	0.290	0.271	0.301	0.300
120	0.460	0.445	0.466	0.462
130	0.675	0.656	0.683	0.680
140	1.01	0.840	0.868	0.864
150	1.65	1.350	1.72	1.70
160	S.T	1.72	S.T	S.T
170		S.T		

* S.T: Sensitive temperature (Bands get outside the chart.)

Table 4 Log I_0/I at different cell thickness and interval time

Parameters	Absorbance at wavenumber 1475 cm^{-1}			Absorbance at wavenumber 1375 cm^{-1}		
	Cell thickness			Interval time		
	Temp. °C	0.05 mm	0.1 mm	0.2 mm	3 min	5 min
80	0.1	0.008	—	0.004	0.009	0.019
90	0.340	0.012	0.006	0.009	0.024	0.044
100	1.61	0.034	0.01	0.014	0.044	0.087
110	S.T	0.040	0.02	0.029	0.081	0.147
120	—	0.070	0.03	0.10	0.128	0.195
130	—	0.150	sample	0.116	0.195	1.195
140	—	0.313	leakage	0.320	0.468	S.T
150	—	0.55	under the effect of expansion	S.T	S.T	—

* S.T. Sensitive temperature (Bands get outside the chart.)

cell material (KBr, AgCl, etc.), cell thickness, and interval between successive spectra.

Results relating to these variables are given in Tables 3 and 4, and are presented graphically in Figs 1–3, from which it may be concluded that the optimum measurement conditions can be achieved by using a KBr cell 0.1 mm in thickness with an interval time of 5 min.

The absorption band intensities for characteristic chemical groups of the oil were found to change on temperature increase. Changes in absorption were investigated for the following bands:

Band, cm^{-1}	Chemical group	Approximate description
3150–2900	aromatic compounds, and CH_3 & CH_2	$\nu_{Ar}\text{-CH}$, $\nu_{as}\text{-CH}_3$, $\nu_s\text{-CH}_3$, $\nu_{as}\text{-CH}_2$ & $\nu_s\text{-CH}_2$
1820–1166	N, O, S hetero compds.	
1610	aromatic compounds	skeletal vibration
1475	CH_2/CH_3	$\beta_s \text{CH}_2$ ($\delta_{as} \text{CH}_3$)
1375	CH_3	$\delta_s \text{CH}_3$
980	naphthenes	$\gamma (= \text{CH})$
850–820	substituted aromatic compounds	$\gamma (= \text{CH})$
720	$\text{---}(\text{CH}_2)_n\text{---}$ where $n \geq 4$	$\beta_{as} \text{CH}_2$

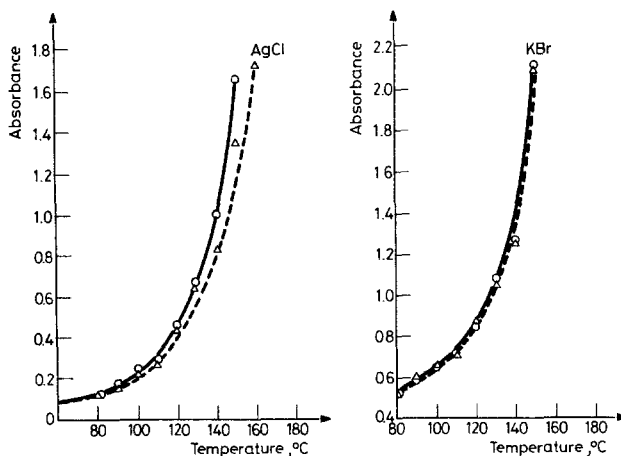


Fig. 1 Comparison between KBr & AgCl cell windows after the 3rd measurement
 - ○ - ○ - 1st measurement; - △ - △ - 3rd measurement

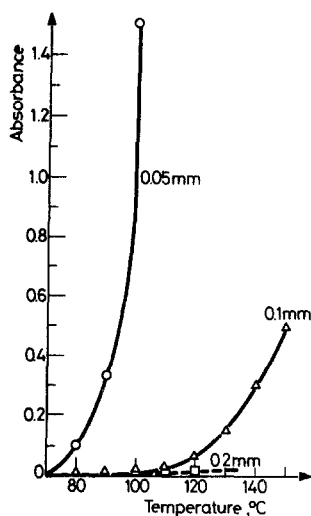


Fig. 2 Effect of thickness on the intensity at different test temperatures

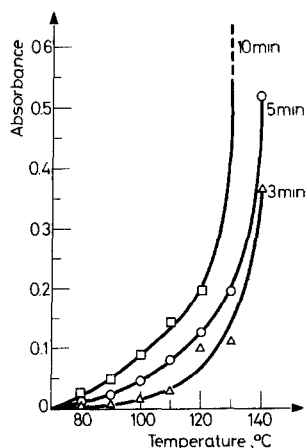


Fig. 3 The relation between interval time and absorbance

The absorptions of the above bands in the temperature range above ambient 25° for the three tested base oil samples 1, 2 and 3 are shown in Figs 4, 5 and 6, respectively. Figure 7 shows that it is possible to compare the different chemical groups within the same base oil (e.g. oil 2). The temperature increase resulted in absorption changes for all the bands, but at different rates. From these Figures it is possible to draw the following conclusions:

A) Paraffinic hydrocarbons

1. The band at 720 cm^{-1} (for $-(\text{CH}_2)_n-$ where $n \geq 4$) indicates that the long paraffinic chains crack into smaller ones. Such chain decomposition increased in a

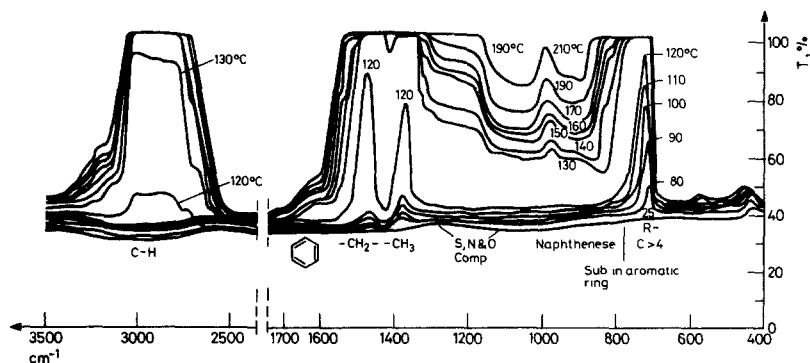


Fig. 4 Spectrum of base oil 1 by using heatable cell of IR spectrophotometric technique

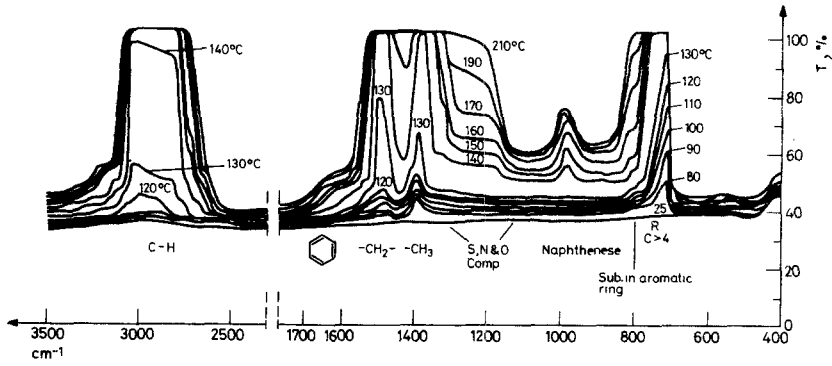


Fig. 5 Spectrum of base oil 2 by using heatable cell of IR spectrophotometric technique

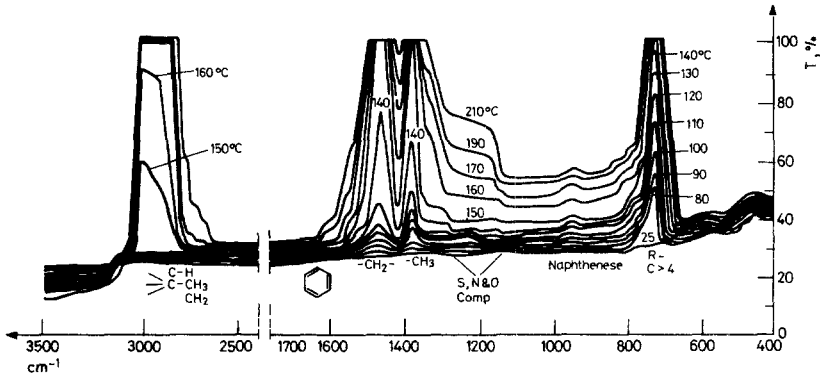


Fig. 6 Spectrum of base oil 3 by using heatable cell of IR spectrophotometric technique

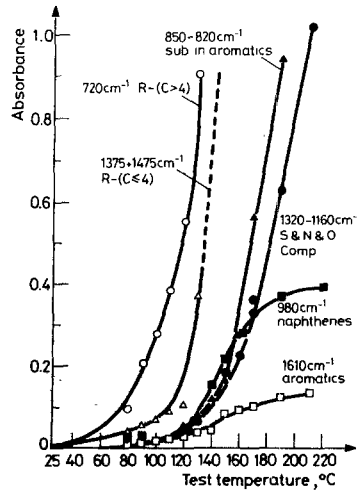


Fig. 7 Change in absorbance of bands representing different chemical groups in tested base oil (sample 2)

stepwise manner on the increase of temperature from 80° to 140°. Above 140°, however, a sudden and sharp change was observed, which is due to a severe chain decomposition.

2. On the increase of temperature from 80° to 130°, the absorptions of the bands at 1375 cm^{-1} (for the $\delta_s \text{CH}_3$ bending mode) and 1475 cm^{-1} (for the $\beta_s \text{CH}_2/\delta_{as} \text{CH}_3$) changed, but at slower rates than for the band at 720 cm^{-1} , i.e. the cracking of the long paraffinic chains is faster than that of the short chains. Such results accord with the organic molecular structure theory [11]. As a result, the percentage of short chains remains nearly constant in the oil.

Above 130°, however, decomposition takes place at faster rates up to 160°, where a sudden change indicates the presence of severe chain decomposition.

3. The increase of temperature up to 140° did not affect the absorption of the band at 2900 cm^{-1} for the C—H group, i.e. decomposition was not marked. Above 140°, however, the absorption started to increase rapidly and at 170° sudden and sharp changes occurred, indicating the occurrence of severe decomposition. The changes in absorption of the tested base oils (samples 1, 2 and 3) up to 160° are presented graphically in Fig. 8, which indicates that the thermal stability increases in the following sequence:

Paraffinic hydrocarbon	Effective temperature range, °C		Thermal stability
	Start	Sensitive temp.	
C > 4	90	140	low
C ≤ 4	100	160	↓
C—H	140	170	high

These differences in thermal stability of the paraffinic hydrocarbons are also in accord with the organic molecular structure theory [11].

B) Naphthenic and aromatic hydrocarbon

The bands at 980 and 1610 cm^{-1} for naphthenic and aromatic hydrocarbons, respectively, remain without any marked change up to 210°. Their absorptions increase steadily in a stepwise way, i.e. without the occurrence of sudden decomposition, but with a relatively high thermal stability for the aromatics in comparison to the naphthenes. These results therefore indicate the higher stability of cyclic hydrocarbons than that of alicyclic hydrocarbons. The higher stability of the aromatic hydrocarbons may be due to the steric nature of the aromatics. The absorption at 850–820 cm^{-1} for substituted aromatic rings supports this conclusion: the thermal stabilities here are between those of paraffinic and aromatic hydrocarbons.

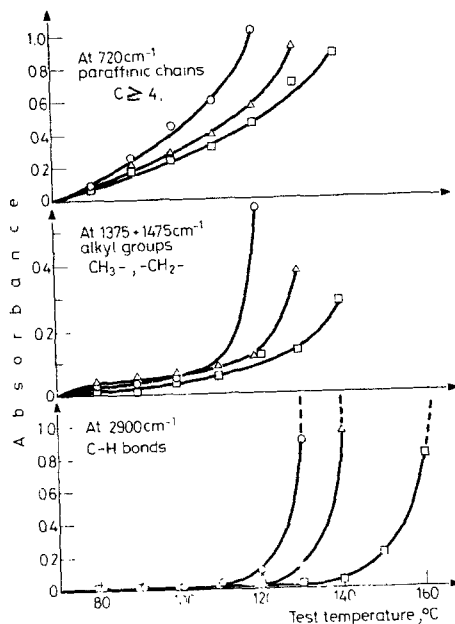


Fig. 8 Thermal stability of paraffinic groups for tested base oils samples by heatable cell of IR procedure; ○ oil 1, △ oil 2, □ oil 3

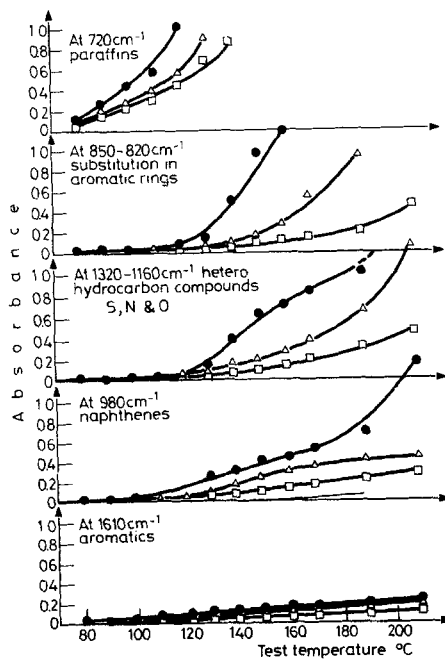


Fig. 9 Thermal stability of different structure groups of base oils 1, 2 & 3 by heatable cell of IR procedure; ● oil 1, △ oil 2, □ oil 3

The absorptions of the 1320–1160 cm^{-1} bands, due to the oxygen, sulphur and nitrogen hetero compounds, change at a steady rate, indicating relatively good thermal stability up to 210°.

The unresolved broad band between 3150 and 2900 cm^{-1} has a contribution from the C—H stretching vibrations of aromatic compounds, and hence the absorption measured in this region is not exactly proportional to the amount of paraffinic hydrocarbons.

C) Comparative evaluation of thermal stabilities of tested base oils

The changes in absorption in the temperature range from ambient to 210° for the tested base oil samples (1, 2 and 3) are shown in Fig. 9, which clearly illustrates the differences in their thermal stabilities.

These results suggest the following sequence of thermal stability of the different hydrocarbon groups:

Hydrocarbon group	Effective temperature range, °C		Thermal stability
	Start	Sensitive temp.	
Paraffinic hydrocarbons	90	170	low ↓ high
Substituted aromatic hydrocarbons	150	190	
Hetero hydrocarbon compounds	150	210	
Naphthenic hydrocarbons	150	above 210	
Aromatic hydrocarbons	160	above 210	

However, a comparative evaluation of the thermal stabilities of different base oils cannot be interpreted without taking into consideration the chemical compositions of the oils. Such an investigation is beyond the scope of the present work and will be discussed in a later paper.

Procedure precision

As concerns the precision limits of the IR spectroscopic technique for measurement of the thermal stabilities of base oils, one sample (oil 3) was tested several times by the same operator under the mentioned conditions Table 2. Standard deviation equations were applied to the results to measure the variance.

The standard deviation of the rate of change in absorption at the different test temperatures was found to be $\pm 1.5\%$ of the mean value, while that of the sensitive temperatures for the paraffinic bands was $\pm 3.26\%$ of the mean value.

Application of thermal stability procedure to base oil additives

The developed IR thermal stability procedure was applied to base oil containing zinc dialkyl dithiophosphate (ZDDP) as an antioxidant additive. The results obtained are illustrated in Figs 10 and 11, and can be summarized as follows:

Chemical group	Effective temperature range, °C		Thermal stability
	Start	Sensitive temp.	
Paraffinic compd.			
C > 4	80	140	low ↓ high
C ≤ 4	90	160	
C—H	160	200	
P—O—C	140	200	
P—C	80	above test range	
P—S	100	above test range	

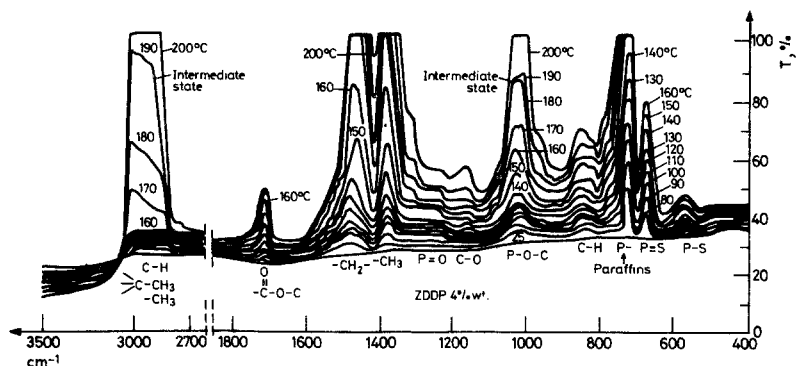


Fig. 10 Spectrum of 4 % wt. ZDDP in base oil 2 by using heatable cell of IR spectrophotometric technique

The bands at 720 cm^{-1} , $1475\text{--}1375\text{ cm}^{-1}$ and 2900 cm^{-1} , representing long paraffinic chains, paraffinic chains with $C \leq 4$, and the C—H group, respectively, were observed to be affected by temperature increase in the same way as for the base oils. The C—H group, however, proved somewhat more thermally stable. This may be attributed to the ZDDP additive, in which there are no long paraffinic chains. The band at 1020 cm^{-1} for the P—O—C group of the ZDDP was affected by temperature between 140° and 200° , above which decomposition takes place.

The bands at 668 cm^{-1} and 544 cm^{-1} , representing the P=S and P—S, respectively, of the ZDDP additive were affected by temperature increase, but at a

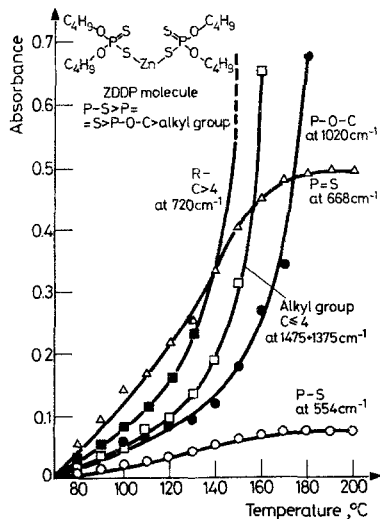


Fig. 11 Comparison between thermal stability of ZDDP chemical groups by heatable cell of IR procedure

temperature lower than that for the P—O—C group. Decomposition did not occur in the test temperature range.

Accordingly, this developed IR technique can be applied to investigate the thermal behaviour of the chemical groups for both base oils and their additives.

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Zusammenfassung — Ziel der Arbeit ist die Untersuchung der thermischen Stabilität von Ölen und deren Additiven bei Temperaturen bis zu 250 °C. Die angewandte Technik beruht auf der Verfolgung der bei verschiedenen Temperaturen eintretenden Veränderungen der Infrarotspektren der getesteten Proben. Die Probe wird in eine spezielle, auf unterschiedliche Temperaturen aufheizbare IR-Zelle eingefüllt. Die Zelle wird zunächst direkt auf 80 °C aufgeheizt, danach wird in Abständen von 10 °C je ein Spektrum aufgenommen, bis eine Temperatur von 250 °C erreicht ist. Die Referenzzelle wird ebenfalls mit der zu untersuchenden Probe gefüllt, jedoch nicht aufgeheizt. Bemerkenswerte und sich klar unterscheidende Veränderungen in der Intensität von einigen, charakteristischen Gruppen chemischer Verbindungen zuzuordnenden Banden wurden beobachtet. Diese Veränderungen gehen zunächst langsam vor sich, werden dann aber bei spezifischen Temperaturen sehr schnell. Das Ausmaß dieser Veränderungen und die spezifischen Temperaturen unterscheiden sich für die verschiedenen Gruppen chemischer Verbindungen. Die thermische Stabilität nimmt in der Reihenfolge Aromaten > Naphthene > Heteroverbindungen > substituierte Aromaten > Paraffine ab. Ein Antioxidant-Additiv des Zinkdialkyldithiophosphat-Typs wurde ebenfalls getestet und bewertet.

Резюме — Исследование термоустойчивости основных компонентов смазочных масел и присадок к ним проведено до температуры 250°. Метод основан на установлении изменений в ИК спектрах образцов, измеренных при различных температурах. Образцы инжестировались в специальную инфракрасную кювету с регулируемой температурой нагрева. Ячейка нагревалась сначала до 80°, а затем через каждые 10° снимались ИК спектры вплоть до температуры 250°. В качестве сравнения служил тот же образец, ИК спектр которого измерялся при комнатной температуре. Изменение поглощения характеристических групп, едва происходящее при начальных температурах нагрева, очень быстро происходило при повышении температуры. Установлено, что степень таких изменений и температуры, при которых они происходят, являются различными для каждой химической группировки. Термоустойчивость таких химических групп уменьшается в ряду ароматические > нафтенны > гетеросоединения > замещенные ароматические > парафины. Проведено также испытание и оценка диалкилди-тиофосфата цинка, используемого в качестве антиокислителя.