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TESTING THE THERMOOXIDATION OF LUBRICATING OILS VIA DIFFERENTIAL THERMAL ANALYSIS

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Two DTA programmes have been developed to differentiate between the thermooxidation stabilities of lubricating oils. Measurements were carried out either by heating the oil sample at a rate of 10 deg/min (direct programme) or by keeping it at 250° (isothermal programme). The selected optimum conditions for these two programmes included the use of 40 mg of sample under oxygen at a flow rate of 150 cm^3/min until oxodegradation of the sample. These conditions were found to give precise and repeatable results. The procedures can be recommended as simple and fast quality control methods.

Thermooxidation parameters from the DTA curves were correlated with results from the standard routine method IP 306.

Evaluation of the thermooxidation stabilities of lubricating oils is usually carried out via either standard routine methods [1] or differential scanning calorimetry (DSC) techniques [2–8].

Most of the routine methods require a long working time (12–1000 h) and a large sample size (up to 4.55 l), and they generally have low limits of precision. The temperature range for these methods is around 95–200°, which does not represent the actual engine conditions. Other routine methods, e.g. involving measurement of viscosity, acidity, sludge content, etc., also have to be carried out in order to evaluate the thermooxidation stabilities of the tested oils. The equipment necessary for these routine methods is seldom used for other tests, which means a need for large investment and skilled operators.

As regards the developed DSC techniques [2–8], their main goals were to measure the oil decomposition peak onset temperatures and to correlate them with engine performance results. DSC is generally fast and precise, and requires only a few mg of the tested sample [3–4]. On the other hand, differential thermal analysis (DTA) has the same merits and is also capable of providing much valuable information about many organic products [9–11].

The work presented in this paper is aimed at finding the optimum DTA

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conditions for measuring the thermooxidation stabilities of lubricating oils. The correlation between the DTA parameters and the results from the routine method IP 306 will be examined.

Experimental

All measurements were carried out on a Stanton Redcroft 671 B differential analyser. The tested oil samples were kept on the DTA porcelain pan under a flow of oxygen. Al_2O_3 was loaded into the other pan as a reference material. The following two programmes were developed:

a) The direct programme, involving heating of the sample at a constant heating rate (2, 5, 10 or 15 deg/min).

b) The isothermal programme, in which the sample is kept at a constant temperature (150, 200, 250 or 300°).

Selection of the optimum conditions was also made through variation of the sample size (10, 20, 30, 40 or 50 mg) and the oxygen flow rate (75, 100, 125, 150 or 200 cm^3/min).

Both programmes were continued until complete decomposition of the samples tested. Changes in the sample energies were recorded as exothermic peaks in the DTA curves. Infrared (IR) spectra of oxidized samples were recorded to assess the extent of oxidation. Two different lubricating oils (oils 1 and 2; Table 1) were selected to establish the optimum working conditions.

A microcomputer with a statistical application module was used to evaluate the degree of correlation between the DTA results and those obtained with the standard routine method IP 306, the measuring conditions of which are listed in

Table 1 Analysis figuses for lubricating oils 1 and 2

Oil no.	1	2
Specific gravity	0.8815	0.8855
Colour	2	2.5
Kinematic viscosity @		
40 °C, c.St.	103.6	55.6
100 °C, c.St.	11.34	7.43
Viscosity index	95	93
Pour point, °C	−6	−6
Conradson carbon, %wt.	0.011	0.008
Ash, %wt.	nil	nil
Total acid no., mg KOH/g	0.03	0.03
Molecular weight	510	450

Table 2. In this method, the extent of oil oxidation is estimated in terms of the percentage of total oxidation products (% TOP). To evaluate the degree of confidence and magnitude of generalization for such a correlation, eight different lubricating oil samples (oils 3–10; Table 3) were tested via both the DTA and the IP 306 method.

Table 2 Measurement conditions for standard routine method IP 306

Test temperature, °C	120
Duration, h	48
Sample size, g	25
O_2 flow rate, l/h	1

Table 3 Analysis figures for lubricating oils 3–10

Oil no.	3	4	5	6	7	8	9	10
specific gravity	0.8818	0.8862	0.8231	0.8820	0.8860	0.8890	0.8850	0.8840
Conradson carbon, %wt.	0.013	0.029	0.2	0.014	0.039	0.112	0.281	0.014
kinematic viscosity at								
40 °C, c.St.	106.7	147.92	194,2	98.24	141.92	199.44	215.6	82.57
100 °C, c.St.	11.5	14.32	17.13	10.82	13.84	17.34	18.38	9.67
viscosity index	94	94	94	93	94	93	94	94
molecular weight	522	572	635	505	553	613	670	488

Results and discussion

A. The direct programme

When a lubricating oil is heated in DTA at a constant heating rate and under a flow of oxygen, two or more exothermic peaks are recorded. Figure 1 is a model DTA curve for such a direct programme.

Generally, such a DTA curve can be regarded as a fingerpring of the oil sample tested. Valuable qualitative and quantitative data can be extracted from it.

To find the optimum conditions via the direct programme, attention was paid to the following parameters: sample size, heating rate and oxygen flow rate; the DTA curves obtained are shown in Figs 2–4. It is possible to conclude that the optimum measurement conditions, which give the best resolution, peak shape and response, are as follows:

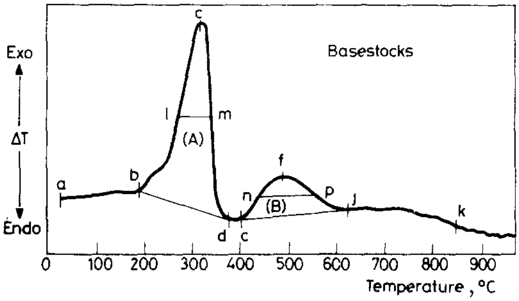

Fig. 1 A model DTA curve for thermooxidation of lubricating oils according to the direct programme. ab: initial heating stage; bcd: 1st exothermic peak; efj: 2nd exothermic; jk: combustion stage; b and e: on-set temperatures; C and F: maximum peak temperatures; d and J: minimum peak temperatures; (A) and (B): peak areas

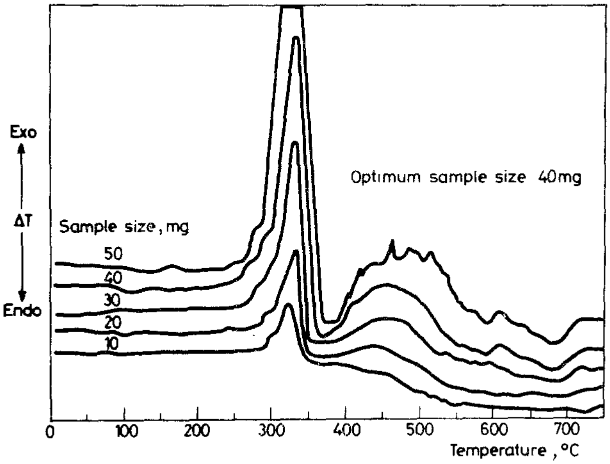

Fig. 2 Effect of change in sample size of lubricating oil sample-DTA direct programme. Heating rate: 10 deg/min; O_2 flow rate: 150 cm^3/min; Chart speed: 2 mm/min

sample size: 40 mg (Fig. 2);
heating rate: 10 deg/min (Fig. 3);
oxygen flow rate: 150 cm^3/min (Fig. 4).

When oils 1 and 2 (Table 1) were tested under these conditions, the two DTA curves presented in Fig. 5 were obtained. The DTA parameters for the two oils according to these curves are listed in Table 4. From these results, it is clear that the selected measuring conditions can differentiate between the thermooxidative stabilities of these two oils. While high peak temperatures were recorded for oil 1, the trend with the peak areas was the opposite. Such differences might be due to the

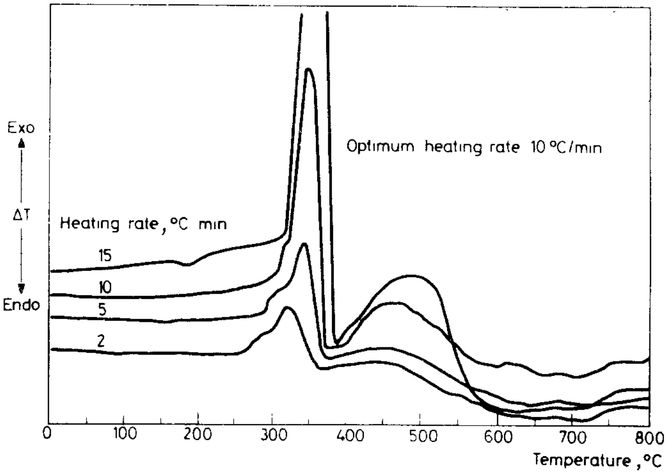

Fig. 3 Effect of change in heating rate-DTA direct programme. Sample size: 40 mg; O_2 flow rate: 150 cm³/min; Chart speed: 2 mm/min

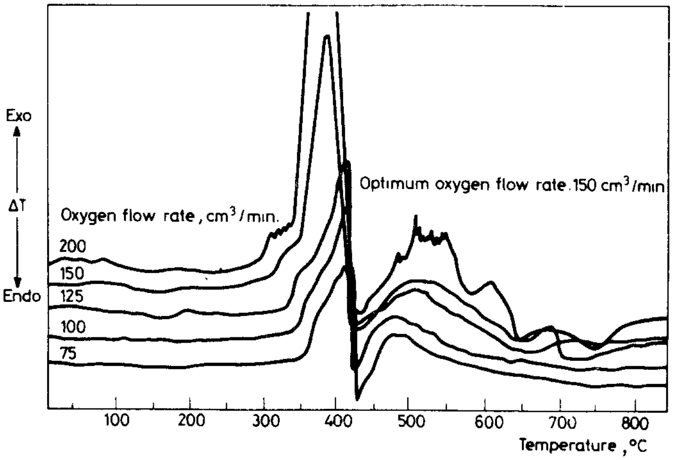

Fig. 4 Effect of change in oxygen flow rate-DTA direct programme. Heating rate: 10 deg/min; Sample size; 40 mg; Chart speed: 2 mm/min

characteristic behaviour of oil 1 in comparison to oil 2 (e.g. oil 1 has a higher viscosity and molecular weight). Further, the tails of the two curves at high temperatures (above 600°) are completely different, with the possibility of high residue formation, especially for oil 2. In general, it is possible to conclude that oil 1 has a higher thermooxidation stability than oil 2.

Figure 6 presents the IR spectra of the two oils after oxidation in DTA, just after the first exothermic peak (i.e. at point P in Fig. 5). The absorbance by the

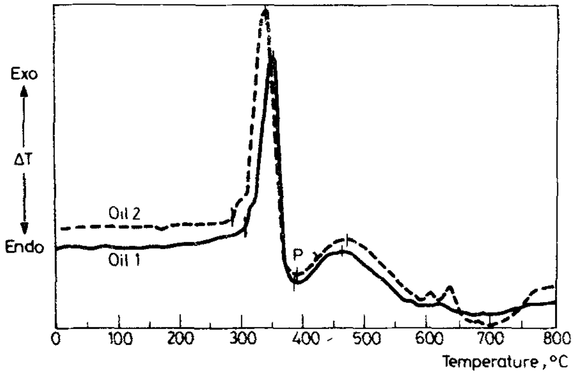

Fig. 5 Thermooxidation behaviour for oils 1 and 2 (Table 1) on the DTA-Via the direct programme. Heating rate: 10 deg/min; Sample size: 40 mg; O_2 flow rate: 150 cm^3/min; Chart speed: 2 mm/min

Table 4 DTA parameters for oils 1 and 2 via direct programme

Parameter	Oil 1	Oil 2
First exothermic peak		
Peak area, mm^2	1005.4	1356.1
Peak onset temperature, °C	300	279
Peak maximum temperature, °C	360	345
Peak minimum temperature, °C	390	385
Peak half-width, mm	9	11.5
Second exothermic peak		
Peak area, mm^2	652.7	914.2
Peak onset temperature, °C	395	390
Peak maximum temperature, °C	466	475
Peak minimum temperature, °C	566	584
Peak half-width, mm	30	39

oxygenated compounds at 1300–1100 cm^{-1} and 1825–1720 cm^{-1} is higher for oil 2 than for oil 1, which supports the low thermooxidation stability of oil 2.

From these results, it is clear that the developed procedure is capable of differentiating between lubricating oils within a short measuring time (80 min). The combination of DTA and IR can help greatly in evaluating the thermooxidation stabilities of lubricating oils.

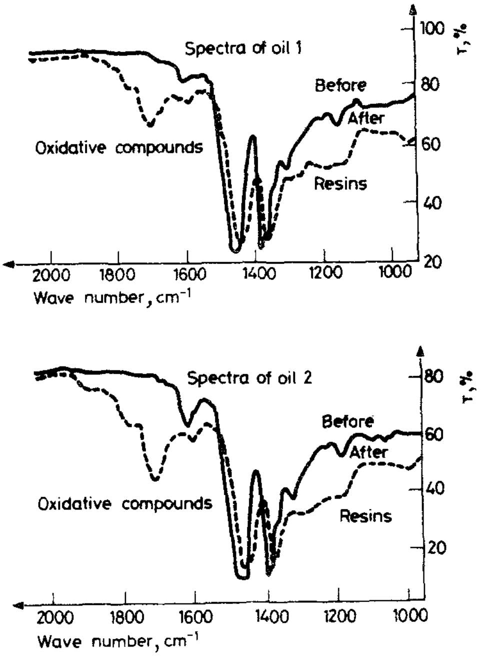

Fig. 6 Infrared spectra before and after oxidation for oils 1 and 2 on the DTA according to the direct programme

B. The isothermal programme

When a lubricating oil sample is oxidized in DTA at a constant temperature and under suitable measuring conditions, there is expected to be a long induction period before oil breakdown. Figure 7 depicts a typical model of oil thermooxidation behaviour in the isothermal programme.

To find a suitable temperature at which to run the isothermal programme, DTA trials were carried at 150, 200, 250 and 300°. Other conditions were typical of those selected in the direct programme. The curves obtained are shown in Fig. 8, which

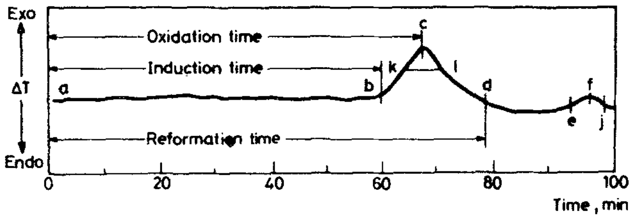

Fig. 7 A model DTA curve for thermooxidation of lubricating oils according to isothermal programme. bcd: 1st exothermic peak, efj: 2nd exothermic peak, kl: 1st half peak width

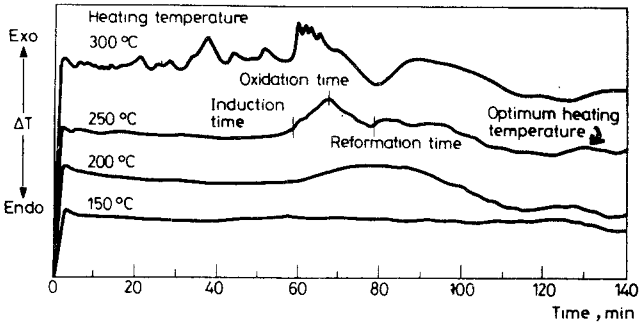

Fig. 8 Effect of change in heating temperature-DTA isothermal programme. Sample size: 40 mg; heating rate: 10 deg/min; O_2 flow rate: 150 cm^3/min; chart speed: 2 mm/min

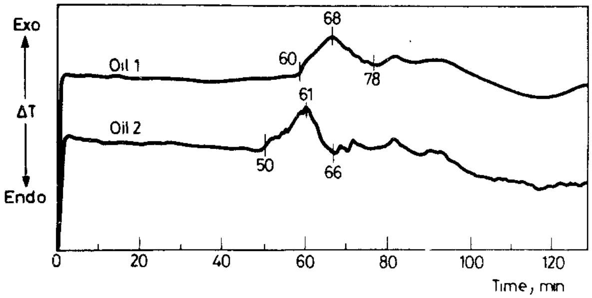

Fig. 9 Thermooxidation behaviour for oils 1 and 2 on the DTA via the isothermal programme. Sample size: 40 mg; heating rate: 10 deg/min; O_2 flow rate: 150 cm^3/min; chart speed: 2 mm/min

indicates that the best resolution and peak shape result at 250°. At 150 and 200° the oxidation stability is relatively high, with a long induction period, while at 300° the rate of change due to thermooxidation and evaporation is very high and the DTA curve contains several small split peaks.

When oils 1 and 2 (Table 1) were tested under the following optimum conditions (sample size 40 mg, heating temperature 250° and oxygen flow rate 150 cm^3/min), the DTA curves shown in Fig. 9 were obtained. The induction times, oxidation times and reformation times for the two oils are listed in Table 5. These results are in

Table 5 DTA parameters for oils 1 and 2 via isothermal programme

Parameter	Oil 1	Oil 2
Induction time, min	60	50
Oxidation time, min	68	61
Reformation time, min	78	66

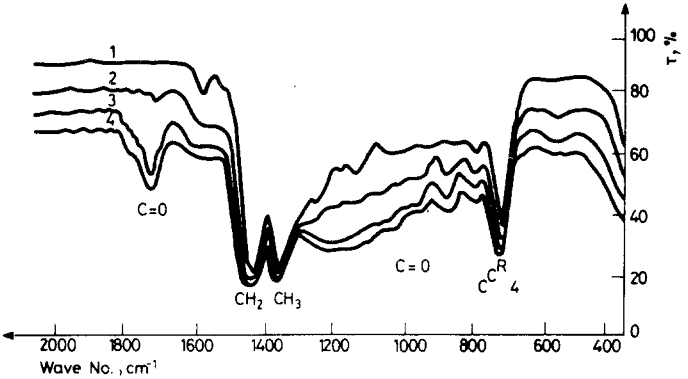

Fig. 10 Infrared spectra for oil (1) at the DTA different oxidation times according to the wave No. and isothermal programme. (1) New oil; (2) oxidized oil at the induction time; (3) oxidized oil at the oxidation time; (4) oxidized oil at the reformation time

good agreement with those obtained with the DTA direct programme and support the high oxidation stability of oil 1.

Figure 10 presents the IR spectra for oil 1 after the induction, oxidation and reformation times (as defined in Fig. 7). It is clear that the IR absorbance at 1825–1720 and 1300–1100 cm^{-1} (i.e. due to the oxygenated compounds formed) increased with increase of the oxidation time. During the induction time the sample could be considered stable, but at the oxidation time fast degradation occurred and continued at the reformation time. Actually, after the oxidation times there was no practical benefit from continuation of the test. The IR absorbance at 1720 cm^{-1} showed that the oxygenated compounds formed at the reformation time were lower than those formed at the oxidation time.

The recommended optimum conditions for both the direct and the isothermal programme are listed in Table 6.

Table 6 Optimum conditions for DTA direct and isothermal programmes

Parameter	Direct	Isothermal
sample size, mg	40	40
heating rate, deg/min	10	10
test temperature, °C	up to 800°	constant 250°
oxygen flow rate, cm^3/min	150	150
chart speed, mm/min	2	2

C. Precision limits and degree of sensitivity

The precision limits for the two developed programmes (i.e. direct and isothermal) were examined by testing oil 1 ten times under the optimum conditions (Table 6) by the same operator. The data obtained were substituted into the standard deviation equation. The calculated precision limits for the different DTA parameters are listed in Table 7. They reveal the acceptable accuracy and high precision of the two developed programmes.

Table 7 Precision limits for different DTA parameters

Parameter	Precision limits from the mean results	
	direct programme	isothermal programme
peak area, mm^2	±1.8%	—
peak half-width, mm	±1.9%	—
peak onset temperature, °C	±1.5%	—
peak maximum temp., °C	±1.8%	—
peak minimum temp., °C	±1.8%	—
induction time, min	—	±1.5%
oxidation time, min	—	±1.5%
reformation, min	—	±2.5%

D. Correlation with the standard routine method IP 306

DTA measurements were carried out on different lubricating oils (oils 3–10; Table 3) with both the direct and the isothermal programme. The results obtained are listed in Table 8, together with those obtained with the standard routine method IP 306. The equations for the degree of correlation between these results are listed in Table 9, where the IP 306 results are represented by Y and the DTA results by X. The correlation coefficients R^2 and F factors for the derived equations are also listed in Table 9.

According to these equations the best degrees of correlation are shown between

a) the IP 306 result (% TOP) with the onset temperature of the first exothermic peak (direct programme) at a confidence level >99.9% and $R^2 = 0.924$;

b) the IP 306 result (% TOP) with the induction time (isothermal programme) at a confidence level >97.5% and $R^2 = 0.85$. Other equations represent different lower degrees of correlation.

Consequently, it is possible to predict the IP 306 results from the DTA parameters. The measured total oxidation products (% TOP) are presented in Figs

Table 8 DTA results for different base oils against those obtained from the standard routine method IP 306

Oil no.	3	4	5	6	7	8	9	10
A. *Direct programme*								
First exothermic peak								
Peak area, mm^2	1750	1872	1990	1517	1517	1653	2066	1507
Peak half width, mm	9.5	10	11	8	8.5	9.5	12	9.0
Peak onset temperature, °C	290	270	255	300	280	270	260	295
Peak maximum temperature. °C	370	355	342	372	365	350	340	370
Peak minimum temperature, °C	390	375	365	390	375	370	375	400
Second exothermic peak								
Peak area, mm^2	931	1019	1172	709	795	839.7	1195	720
Peak half width, mm	93	41	42	35	36	37	42	35
Peak onset temperature, °C	428	415	400	425	425	410	405	440
Peak max. temperature, °C	521	517	514	512	515	517	525	522
Peak min. temperature, °C	610	620	628	600	695	525	645	605
B. Isothermal programme								
First exothermic peak								
Induction time, min	60	50	40	65	55	50	43	62
Oxidation time, min	68	61	50	76	67	62	52	73
Reformation time, min	78	72	60	86	78	73	63	83
C. Standard IP 306 method								
TOP %	1.5	2.5	2.95	1.5	1.75	2.5	2.9	1.7

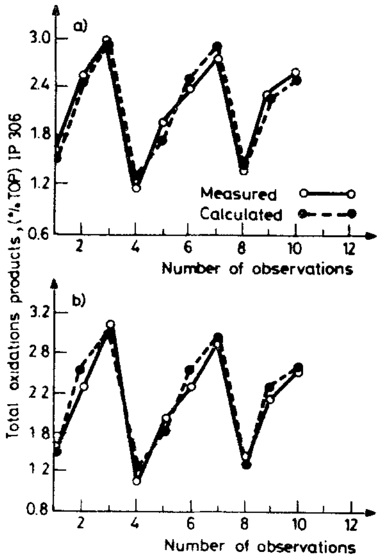

Fig. 11 Measured and calculated total oxidation products (%TOP)–IP 306. A) Calculated from the DTA on-set temperature 1st exothermic peak-direct programme; B) calculated from the DTA induction time-isothermal programme

Table 9 Correlation equations for DTA and IP 306 parameters

Y	Total oxidation products % TOP–IP 306			
X	Derived equation	R^2	F	% confidence
DTA direct programme				
a. First exothermic peak				
Peak area, mm^2	$Y=0.001X-2.254$	0.527	14.5	>95
Peak half-width, mm	$Y=0.491X-2.73$	0.67	26.76	>95
Onset temperature, °C	$Y=-0.04X+12.96$	0.924	153.29	>99.9
Peak maximum temperature, °C	$Y=0.05X+19.12$	0.84	73.29	>97.5
Peak minimum temperature, °C	$Y=-0.048X+20.42$	0.722	33.92	>95
b. *Second exothermic peak*				
Peak area, mm^2	$Y=0.001X-0.75$	0.69	29	>95
Peak half-width, mm	$Y=0.198X-5.16$	0.68	27.6	>95
Onset temperature, °C	$Y=-0.044X+20.72$	0.716	49.33	>97.5
Peak maximum temperature, °C	$Y=0.001X+7.06$	0.001	0.067	low
Peak minimum temperature, °C	$Y=0.001X+1.17$	0.001	0.07	low
DTA isothermal programme				
Induction time, min	$Y=-0.08X+6.361$	0.85	71.2	>97.5
Oxidation time, min	$Y=-0.053X+5.44$	0.52	14.313	>95
Reformation time, min	$Y=-0.062X-6.73$	0.74	37.65	>97.5

11*A* and *B* against the calculated values derived from the DTA peak onset temperatures and induction times.

Conclusions

Direct and isothermal DTA thermooxidation programmes were developed to test lubricating oils. The optimum measuring conditions for these two programmes were established, and were found to give precise results with narrow precision limits.

The correlation between the DTA results and those from the standard routine method IP 306 was found to be satisfactory. Consequently, it is possible to predict the results of the IP 306 method directly from the DTA parameters.

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Zusammenfassung — Zwei DTA-Programme wurden zur Differenzierung zwischen Thermooxydationsstabilitäten von Schmierölen entwickelt. Die Messungen wurden entweder durch Aufheizen des Öls mit einer Geschwindigkeit von 10 grd/min (direktes Programm) oder durch thermische Behandlung bei 250 °C (isothermes Programm) ausgeführt. Ausgewählte optimale Bedingungen für diese zwei Programme sind die Verwendung von 40 mg Probe in einem Sauerstoffstrom von 150 cm^3/min bis zum oxydativen Abbau der Probe. Diese Bedingungen ergeben genaue und reproduzierbare Resultate. Die Prozedur kann als einfache und schnelle Qualitätskonstrollmethode empfohlen werden. Durch DTA erhaltene Thermooxydationsparameter werden mit durch die Standardroutinemethode IP 306 erhaltenen Ergebnissen verglichen.

Резюме — С целью определения устойчивости смазочных масел к термоокислению, были разработаны две ДТА-программы. Измерения проводились путем нагревания масел со скоростью 10°/мин. (прямая программа) или выдерживанием образца при температуре 250° (изотермическая программа). Оптимальные условия для этих двух программ включали использование 40 г образца в атмосфере кислорода при скорости потока 150 см^3/мин. до полного окисления. Такие условия позволяют получать точные и воспроизводимые результаты. Разработанные методики могут быть рекомендованы в качестве простых и быстрых качественных методов контроля. Параметры реакции термоокисления, найденные из кривых ДТА, коррелировались с результатами, полученными на основе стандартного метода ИП–306.