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THERMOGRAVIMETRIC EVALUATION OF A MOTOR OIL DURING PERFORMANCE

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ABSTRACT

A simple and rapid thermoanalytical method is described for evaluating the performance of a motor oil in situ which could be used to estimate its usage limit. From thermograms obtained when using selected heating programs, data pertaining to the thermal behavior of motor oil samples withdrawn at different driving distances, their light, middle and residual fractions were studied. Sharp changes were observed indicating fast deterioration when the recommended usage limit set by the manufacturer was approached. It is proposed to introduce this technique as an aid and indicative method in the evaluation of these products during their actual performance.

INTRODUCTION

Engine test methods for the performance evaluation of petroleum products particularly the lubricating oils and fuels, is a well known technique [1]. The customer specification for the purchase of an oil often includes an engine test certificate besides the physical and chemical properties of the lubricant [2].

The technique of using a standard engine as test equipment usually involves running the engine under controlled conditions followed by the elaborate and time consuming methods of evaluating the parameters like bearing weight loss, piston deposits, piston ring condition, oil consumption and oil deterioration due to chemical decomposition, acidity and viscosity changes [3,4].

Recently [5], thermoanalytical techniques have been applied successfully as tools for estimating the stability of petroleum products and has gained the interest of many workers. Differential scanning calorimetry (DSC) has been used extensively [6,7] in determining the thermal stability of lubricating oils and to study the efficiency of a range of additives used in inhibiting their degradation. Thermogravimetry (TG) and differential thermogravimetry (DTG) were also used as methods of assessing the thermal stability of oils, lubricating greases, waxes and crude oils [8,9,10].

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The work discussed in this investigation involved the application of programmed thermogravimetry to samples of a motor oil withdrawn from a car engine driven to increasing distances and reaching the specified limit for its usage set by the manufacturer. Results obtained from this technique pertaining to the lubricating quality of the oil used correlated well with the manufacturer's specification.

EXPERIMENTAL

Samples

A commercial motor oil of grade SAE 30 was purchased from the market. Specifications of this oil are given in Table 1. Its specified limit on the driving distance as recommended by the manufacturer was not to exceed 3000 km.

Apparatus

Thermogravimetric analyses were performed on a Heraeus TA 500 system. A 1980 Datsun automobile model 180B with its milage indicator reading 80000 km was used in this investigation. Its engine was cleaned thoroughly and tuned prior to the introduction of the fresh oil.

TABLE 1

Specifications of fresh and spent (3000 km) lubricating oil

Specifications [a]	Fresh oil	Used oil
Viscosity (cSt) at 100°C	10.8	7.5
Specific gravity at 15.6°C	0.89	0.89
Flash point (°C)	230	180
Sulfur content (wt.%)	0.65	0.72
Acid No. (mg KOH/g of sample)	0.04	3.5
Water (wt.%)	0	1.2
Carbon residue (wt.%)	0.05	1.8
Color	dark yellow	black
Lead (ppm)	0	600
Calcium (ppm)	1200	1250
Zinc (ppm)	590	595
Barium (ppm)	350	345
Iron (ppm)	0	150
Vanadium (ppm)	5	5
Aluminum (ppm)	0	0

[a] Measured according to A.S.T.M. methods.

Procedure

Duplicate oil samples were withdrawn from the dipstick hole at 2-min intervals while the engine was running and hot. Samples were taken at the end of each 500 km driving distance and up to 3000 km. The specifications of the spent oil at the end of the test run are also given in Table 1.

Oil samples (5–10 mg) were placed in a platinum crucible of the balance and heated according to the selected heating program in an inert atmosphere of nitrogen gas flowing at 15 cm^3 min^{-1}.

In the non-isothermal measurements, the oil samples were heated between room temperature and 550°C. The heating rate was 100°C min^{-1}. The isothermal measurements involved raising the temperature of the oil samples from room temperature to 300°C and holding isothermal for 2 min, followed by heating to 400°C while maintaining the temperature constant at this level for another 2 min. The heating rate used was again 100°C min^{-1}. All measurements were performed in duplicate.

DISCUSSION OF THE RESULTS

The main features of the non-isothermal and isothermal thermogravimetric curves of the oil samples studied are displayed in Figs. 1 and 2, respectively. The weight loss of the oil under the inert atmosphere of nitrogen gas corresponds mainly to the volatilization of its hydrocarbon constituents, water and other formed compounds.

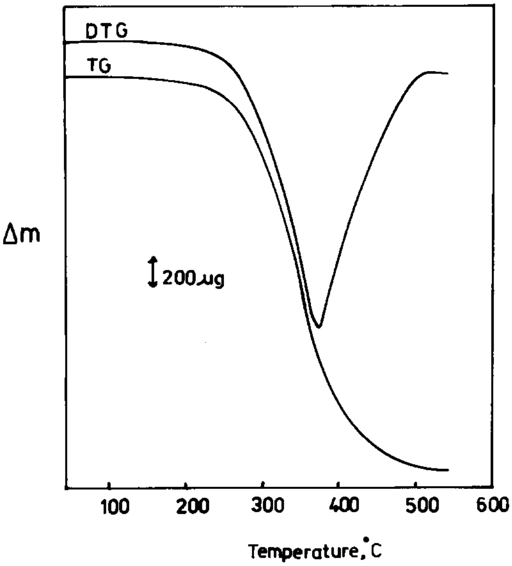

Fig. 1. Representative non-isothermal thermogram of the studied oil samples.

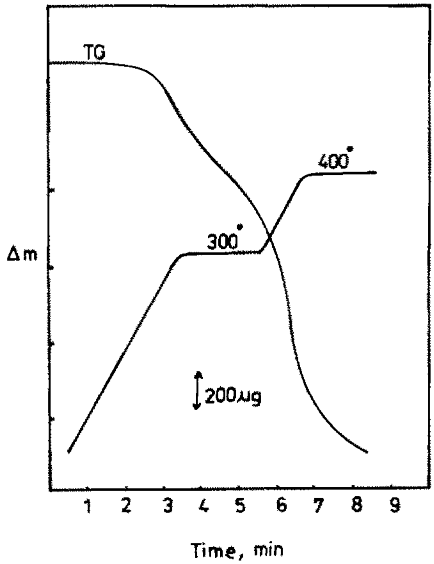

Fig. 2. Representative isothermal thermogram of the studied oil samples.

In the non-isothermal measurements, oil samples underwent volatilization which proceeded with a well-defined single, broad transition starting at about 210°C and terminating at 525°C and indicating a very fast weight loss between 250 and 350°C. A minor weight loss was recorded at about 150°C due to loss of moisture. The initial (T_i), maximum (T_{max}) and final (T_f) temperatures of transition of the major volatilization step which were recorded from the DTG curves are given in Table 2 while the percentages weight lost at 100°C intervals are given in Table 3. The percentage residue by weight remaining at the end of the temperature program for the studied oil samples was about 4.5 to 5.

The thermal data presented are almost identical, thus rendering them insufficient for the purpose of distinguishing between the different oil samples.

TABLE 2

Temperatures of transition of the major volatilization step obtained from the DTG curves for the different oil samples (°C)

Distance travelled (km)	T_i	T_{max}	T_f
0	212	380	520
500	210	375	525
1000	215	375	525
1500	212	375	520
2000	210	370	520
2500	215	370	522
3000	215	378	525

TABLE 3

The percentage weight lost at 100°C intervals for the oil samples obtained from the TG curves of the non-isothermal measurements

Distance travelled (km)	50–150	150–250	250–350	350–450	450–550	Left-over
0	0.5	4.0	50.5	35.0	5.5	4.5
500	0.5	4.0	50.0	35.5	5.5	4.5
1000	0.5	4.1	50.0	35.5	5.3	4.6
1500	0.6	4.2	51.0	33.8	5.8	4.6
2000	0.6	4.1	51.0	34.0	5.7	4.6
2500	0.7	4.1	50.5	34.0	5.8	4.9
3000	0.8	4.3	50.0	34.0	5.9	5.0

Meanwhile, the data extracted from the isothermal curves are given in Table 4. The light fraction referred to as L was the percentage weight loss involved in the temperature range: ambient–300°C including the 2-min holding time. The middle fraction (M) was the percentage weight loss involved after the 2-min isothermal step-up to 400°C including the 2-min holding time at this temperature. The residue, referred to as R, is the amount of product left over at the end of the experimental run. The plots of L, M and R expressed in wt.% against distances travelled (km) are shown in Fig. 3.

It is interesting to observe from Fig. 3 the sharp increase in the light fraction (L) constituents of the motor oil when the running distance exceeded 2500 km. This could be attributed to the depletion of the activity of the additives resulting in the breakdown of the hydrocarbon constituents, and leading to the formation of excessive quantities of smaller molecular weight hydrocarbons. A similar observation was recorded for the middle fraction (M), however, it was reversible and it was recorded as a sharp decrease for this particular fraction over the 2500 km range compensating for the former behavior.

TABLE 4

Thermogravimetric data (wt.%) on the oil samples withdrawn at different distances obtained from the isothermal measurements

Distance travelled (km)	L	M	R
0	34.2	60.5	5.3
500	34.5	60.1	5.4
1000	35.0	58.8	6.2
1500	35.0	58.0	7.0
2000	37.0	55.7	7.3
2500	37.4	54.6	8.0
3000	45.8	44.7	9.5

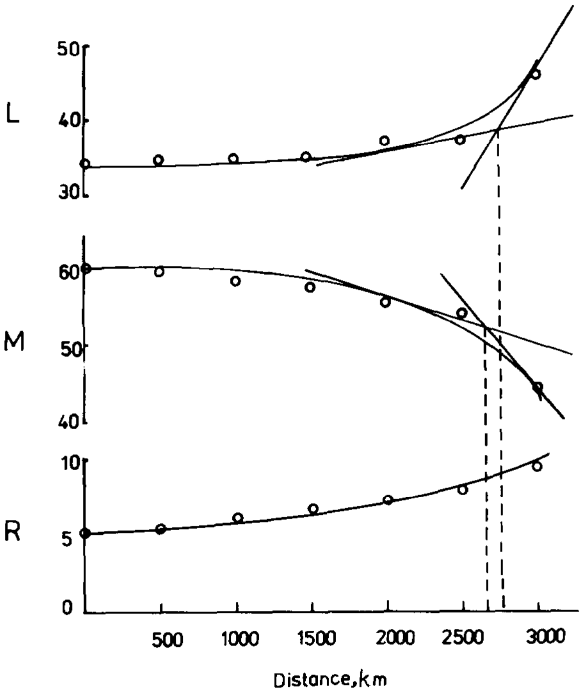

Fig. 3. Plots of L, M and R expressed in percentage by weight against distances travelled (km).

Meanwhile, as expected, a steady increase in the residual fraction (R) was recorded throughout the distance proceeding the first 500 km (Fig. 3) which could be attributed to the gradual accumulation of polymerized high molecular weight hydrocarbons, carbon residue, metals, etc.

Extrapolation of the tangents of L and M curves and evaluation of their intersects yielded somewhat proximate values ranging between 2500–3000 km. These values correlated well with the specified distance limit of 3000 km set by the manufacturer for the usage of this particular oil.

Finally, the thermogravimetric technique employed could be introduced as a supplementary and aiding tool in evaluating the performance of motor oils. More importantly, this technique offers the advantage of being relatively simple, less time-consuming than conventional methods, accurate and using only a small sample size. Further, its applicability can be expanded to cover many types of lubricating oils.

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