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THERMOANALYTICAL INVESTIGATIONS ON LITHIUM STEARATE, LITHIUM 12-HYDROXYSTEARATE AND RELATED GREASES

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TG and DSC techniques proved useful in the study of the thermal properties of lithium stearate, lithium 12-hydroxystearate and related greases. Under an inert atmosphere, the stearates decompose into the oxalate prior to the formation of the carbonate. For the related greases, oil degradation-volatilization shows a discontinuity under ambient conditions, because of oxidation and carboxylic acid formation. The atmosphere and the concentration of the soap affect the chemical kinetics of thermal decomposition of the stearates and the greases.

The use of thermoanalytical methods in the study and the characterization of petroleum products is receiving increasing interest, as they furnish quick data on the stability of these products that are important for application purposes and for design and operation requirements [1, 2].

Lubricating greases which are petroleum-derived products are defined as a solid to semi-fluid dispersion of a thickening agent in a liquid lubricant [3]. The majority of thickeners are metal soaps of long-chain fatty acids. The predominant acid radicals in the metal soaps are stearate and 12-hydroxystearate. The preference for the use of these types of thickeners is due to the fact that greases containing such soaps have exceptional properties [3]. The liquid lubricants which contribute 80 to 95% of the composition are mostly solvent-refined mineral oils.

Various thermoanalytical techniques are employed to study lubricating greases. These include differential thermal analysis and thermogravimetry [4, 5]. The thermal stability of greases is usually governed by the metal soap content and the type of soap used [5].

In the present work, differential scanning calorimetry and TG techniques are used to study the thermal properties of lithium stearate (LS) and lithium 12-

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hydroxystearate (LOHS), as well as related greases. The study involved a kinetic approach to account for the influence of the atmosphere and the concentration of the thickeners on their thermal behaviour.

Experimental

Materials: Commercial lithium stearate and lithium 12-hydroxystearate of 97% purity were obtained from a local refinery. The lubricating oil of grade 60 low viscosity index (LVI) was obtained from the same refinery. Lubricating greases containing 5, 10 and 15 wt.% of the thickener were prepared at elevated temperatures (200°) by dissolving the individual soap in the grade 60 LVI oil. The greases were thoroughly homogenized prior to investigation in the thermal analyser. The homogeneity of a sample was checked by the reproducibility of the thermal curves. Thermal analysis: The TG, DTG and DSC measurements were carried out on a Heraeus TA 500 thermal analyser. TG experiments required 5–8 mg samples, which were placed in platinum crucibles and heated at a rate of 20 deg min^{-1} under static air or dynamic nitrogen atmospheres, using a flow rate of N_2 of 50 ml min^{-1}. For the DSC measurements, samples weighing 3–6 mg were placed in aluminium dishes and heated at a rate of 10 deg min^{-1} under static air or N_2 atmospheres. The reference cell was left empty. Pure tin was used in calibrating the thermal analyser.

Results and discussion

Thermal analysis of LS:

The DSC curves of LS are complex and are very dependent on the atmosphere of heating. The soap undergoes a phase transition in the solid state, between 97 and 115°, with maximum peak temperature at 108°. Another two transitions occur between 180 and 230°, with maxima at 200 and 227° under N_2, and at 213 and 229° under ambient atmosphere. The first transition (108°) is endothermic, regardless of the nature of the atmosphere, whilst the last two depend greatly on the atmosphere (Fig. 1). Recently, Montmitonnet et al. [6] reported that the enthalpy and the peak temperatures of these transitions are dependent on the experimental conditions. They were able to detect a new phase of LS through successive heating and cooling cycles. The dependence of the thermodynamic nature of the last two changes on the atmosphere assumes chemical structural changes, rather than simple physical change. The last process is accompanied by a relatively small weight loss (Fig. 2).

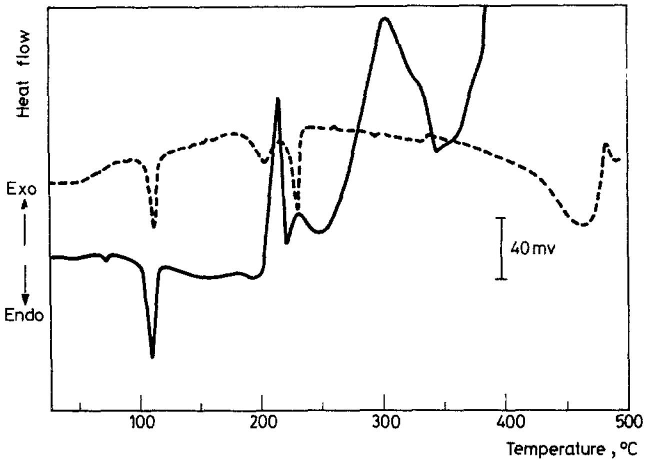

Fig. 1 DSC curves of lithium stearate under air (—) and N_2 (---)

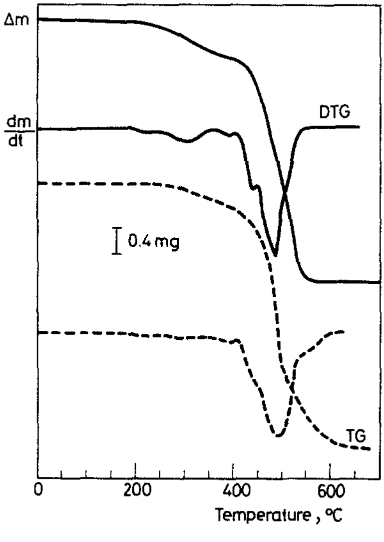

Fig. 2 TG and DTG curves of lithium stearate under air (——) and N_2 (---)

LS undergoes oxidative degradation between 230 and 360° under a static atmosphere and the process is highly exothermic. Under nitrogen, the process is endothermic and occurs between 230 and 415°. The major degradation takes place beyond 415°, where two distinct endothermic processes could be observed in the DSC curve recorded under N_2. The degradation under the static atmosphere was a series of combustion steps. The data extracted from the TG curves (Fig. 2) indicated that the process leads directly to the carbonate at temperatures higher than 545°. On the other hand, lithium oxalate was a possible product under the inert atmosphere. The oxalate decomposes to the carbonate at 550°.

A computer programme [7, 8] was used to estimate the kinetic parameters of the main decomposition process of LS using the TG data. The results are given in Table 1. It is clear from the Table that the decomposition of LS is a second-order reaction, regardless of the nature of the atmosphere. The activation energy attains a value that is 20% greater under the oxidizing atmosphere, because of the expected interaction of the gaseous products with oxygen.

Table 1 Kinetic parameters of thermal decomposition of lithium stearate and lithium 12-hydroxystearate

Parameter	LS		LOHS	
	N_2	Air	N_2	Air
n	1.81	1.78	0.75	0.70
E_a, kJ mol^{-1}	195.4	229.5	46.7	49.1
log z	19.51	20.92	6.04	6.07
R	0.9914	0.9953	0.9975	0.9987

R = correlation coefficient

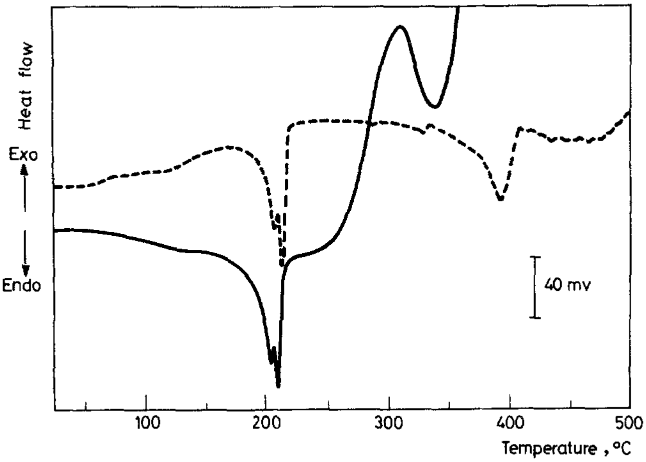

Fig. 3 DSC curves of lithium 12-hydroxystearate under air (——) and N_2 (– – –)

Thermal analysis of LOHS:

The soap dehydrates slowly between 110 and 170° under both atmospheres and loses ~1.5% of its bulk weight. The process is slightly endothermic (Fig. 3). The dehydration is succeeded by slow melting in the range 170–218°. The thermal decomposition occurs in three partially overlapping exothermic steps under ambient atmosphere, at 244–397, 397–450 and 450–550°. The steps involve weight losses of 15.6, 21.3 and 49.9%, respectively. Under nitrogen, the degradation follows an identical route, but the three steps are further segmented and appear as several steps slower in rate than those recorded under air. The last step in particular undergoes a discontinuity at 552°, demonstrating the formation of lithium oxalate prior to the final decomposition the carbonate (556–612°).

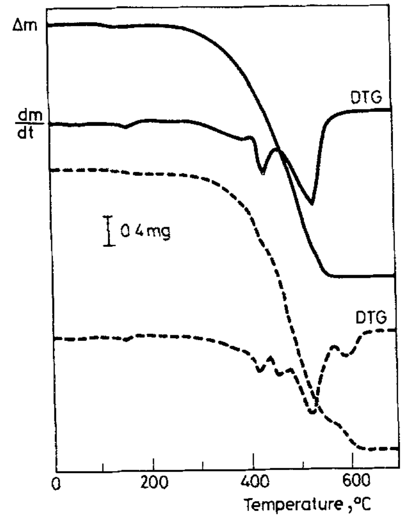

Fig. 4 TG and DTG curves of lithium 12-hydroxystearate under air (——) and N_2 (– – –)

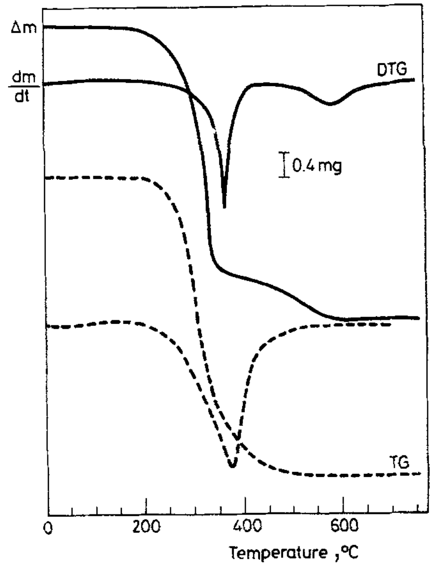

Fig. 5 TG and DTG curves of 60 LVI oil under air (——) and N_2 (– – –)

Similarly, the data extracted from the TG curves (Fig. 4) of the whole decomposition reaction were employed to estimate the kinetic parameters. The results are given in Table 1.

Thermal behaviour of the greases:

The TG curves of the base oil are shown in Fig. 5. It is clear that the oxidative atmosphere causes the oxidation of the oil, and carboxylic acids are formed. This can be the reason for the discontinuity in the oil volatilization under a static atmosphere in comparison with the inert conditions. This difference in thermal behaviour also affected the kinetic parameters, where a noticeable change of the reaction order occurs (Table 2) due to the expected contribution of oxygen to the overall rate equation.

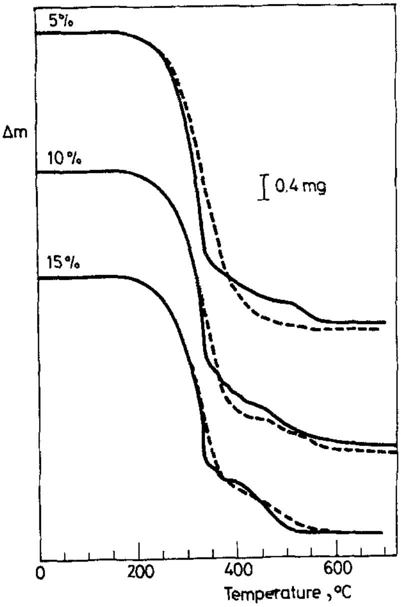

Fig. 6 TG curves of lithium stearate greases under air (——) and N_2 (– – –)

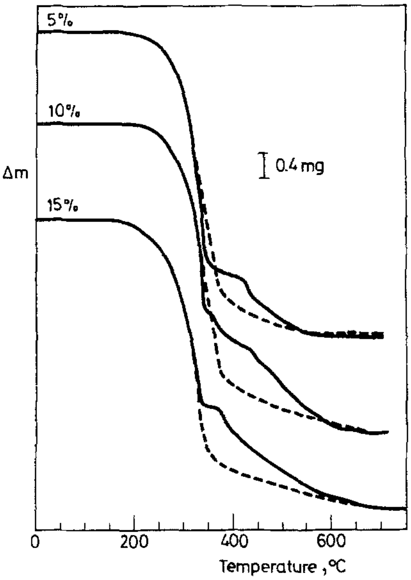

Fig. 7 TG curves of lithium 12-hydroxystearate greases under air (——) and N_2 (– – –)

Table 2 Kinetic parameters of thermal degradation–volatilization of 60 LVI oil

Parameter	N_2	Air
n	1.6	0.9
E_a, kJ mol^{-1}	62.7	60.7
log Z	10.18	8.22
R*	0.9959	0.9916

* R is the correlation coefficient

The main feature of the TG curves of the studied greases (Figs 6 and 7) was the volatilization of the base oil, which begins slowly at 140°, and the weight loss becomes ~1.5% at 200°. The rate of weight loss becomes appreciable above this temperature and reaches a maximum at 332° (DTG peak max.). The process was slower under the inert conditions and attained the maximum rate at 350°. Similar observations on a variety of lubricating greases led us to use the TG data obtained under the inert atmosphere to estimate the content of the base oil [5]. The oxidative atmosphere, however, causes the rapid oxidative volatilization of the oil and lowers the temperature of the maximum rate from 355 down to 330°. The resulting material

Table 3 Kinetic parameters of lithium stearate greases

Parameter	5% soap		10% soap		15% soap	
	N_2	Air	N_2	Air	N_2	Air
n	0.98	0.97	0.78	0.31	1.01	0.51
E_a, kJ mol^{-1}	76.2	68.5	57.9	54.4	55.9	65.6
$\log Z$	9.64	9.44	7.77	7.25	8.23	8.15
R*	0.9979	0.9907	0.9986	0.9981	0.9990	0.9968

* R is the correlation coefficient

Table 4 Kinetic parameters of lithium 12-hydroxystearate greases

Parameter	5% soap		10% soap		15% soap	
	N_2	Air	N_2	Air	N_2	Air
n	1.14	1.39	0.81	0.14	0.84	0.50
E_a, kJ mol^{-1}	60.3	74.9	54.3	48.3	56.9	63.7
$\log Z$	9.02	11.03	7.63	6.47	8.11	8.48
R*	0.9974	0.9899	0.9991	0.9973	0.9988	0.9989

* R is the correlation coefficient

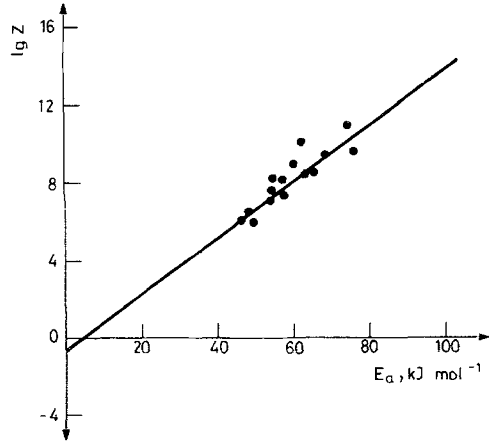

Fig. 8 Plot of kinetic compensation effect

is a complex mixture of freshly-formed carboxylic acids and the already existing soap. The lithium soap did not alter the thermal characteristics much. Figures 6 and 7 indicated that the volatilization of the oil ends smoothly at 475°. Beyond 416°, the TG signals of the greases represent the sum of the effects, the volatilization of the oil and the initial decomposition of the soaps. Calculations of the oil contents of the greases in this case lead to erroneous results unless corrections are made for the amount of soap decomposition.

The principal step in the TG curves was studied kinetically to establish the influence of the increasing concentration of the two soaps on the thermal behaviour of the oil. The kinetic parameters of the volatilization of the greases are listed in Tables 3 and 4. A noticeable change of reaction order can be seen because of the presence of LS in the oil at the percentages studied. The effect of LOHS depends on its percentage in the oil. The Tables show that the influence of the two soaps on the activation energy is low.

The significance of the kinetic treatment of these observations can be tested by estimating the parameters of the compensation effect, a and b. The usual procedure is to plot the pre-exponential factor against the activation energy. Figure 8 shows the compensation effect for the thermal behaviour of the oil and the lithium greases. The parameters of the compensation law [9]:

$$\log z = aE_a + b \tag{1}$$

were calculated from the plot and found to be

$$a = 0.1416\ \mathrm{mol \cdot kJ^{-1}} \text{ and } b = -0.8.$$

These values compare well with the published ranges of compensation parameters [10]. The kinetics of the thermal volatilization of lithium greases are governed by a linear compensation law of type (1).

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Zusammenfassung — TG- und DSC-Techniken haben sich als nützlich für die Untersuchung der thermischen Eigenschaften von Lithiumstearat, Lithium-12-hydroxystearat und der entsprechenden Schmierfette erwiesen. In inerter Atmosphäre zersetzen sich die Stearate über Oxalate als Zwischenprodukt zu Carbonaten. Under Umgebungsbedingungen verläuft die Ölzersetzung-

Verflüchtigung der entsprechenden Schmierfette wegen der Oxydation und der Bildung von Carboxylsäure diskontinuierlich. Atmosphäre und Konzentration der Seife beeinflussen die Kinetik der thermischen Zersetzung der Stearate und der entsprechenden Schmierfette.

Резюме — Показано применение методов ТГ и ДСК для изучения термических свойств стеарата лития, 12-оксистеарата лития и родственных жиров. В инертной атмосфере стеараты разлагаются до оксалатов, предшествующих образованию карбонатов. В случае жиров процессы разложения и улетучивания масел протекают непрерывно, вследствии окисления и образования карбоновой кислоты. Тип атмосферы и концентрация мыла затрагивают химическую кинетику термического разложения стеаратов и жиров.