

Thermogravimetric Study of Lubricating Greases

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ABSTRACT. Thermogravimetric analysis under inert atmosphere has been applied as a unique method of studying lubricating greases of various compositions. While this quick method of analysis proved useful in distinguishing between lubricating greases, it also provided significant information on the relative composition of these products.

A lubricating grease is defined as a solid to semi-fluid product of a dispersion of a thickening agent in a liquid lubricant (Boner 1976). The majority of thickeners are metal soaps of long chain fatty acids. The liquid lubricant which constitutes 80 to 95% of the composition are mostly solvent refined mineral oils. The type of the lubricating grease determines the degree of refinement of the mineral oil.

Thermoanalytical techniques are useful in the evaluation and characterisation of lubricating greases. Thermal stability, hardening and accurate determination of transition temperatures are the main features present in the practical application of thermogravimetry (TG) and differential thermal analysis (DTA) to this field (Noel 1972). The thermal stability of greases is governed by metal soap contents and this method of analysis has been applied in distinguishing between calcium-based greases (Institute of Petroleum 1976).

In the present work, thermogravimetry is applied as a unique method of studying lubricating greases of various compositions and in distinguishing between them. The TG curves are also used in estimating the oil composition of these products.

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Experimental

Apparatus

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded simultaneously on a Heraeus TA 500 thermal analyser. The grease samples weighing 5-20 mg were placed in a standard platinum crucible and heated at a rate of $20^{\circ}\text{C min}^{-1}$ under a flowing atmosphere of nitrogen gas.

Materials

Lubricating greases were prepared at elevated temperature by dissolving the required thickening agent in suitable mineral oil (Al-Sammerrai and Said 1984). The actual thickening agents input are shown in Table 1. The lubricating greases were thoroughly homogenised prior to examination in the thermal analyser.

Results and Discussion

The thermal stability of a grease is greatly dependent on the thickening agent used. The TG and DTG curves of the greases based on the low viscosity index grade 60 oil (60 LVI) together with the thermogram of the individual oil itself are shown in Fig. 1 and 2. Figure 3 shows the thermogram of the hydrocarbon grease together with the thermograms of its oil constituent, *i.e.* the high viscosity index grade 60 (60 HVI) and the bright stock grade 150 oil. The thermograms corres-

Table 1. The estimated composition of the lubricating greases.

Type of grease	Oil %	
	estimated	actual
Calcium stearate grease	98.97	99-98
Aluminium stearate grease	95.64	95.0
Sodium based grease	75.0 ^a	78.0
Polymer grease	96.0 ^b	94-96
Hydrocarbon grease	64.8 ^c	55-65
Complex calcium grease	77.42	75.0
Normal calcium grease	83.26	82.5

a. partial decomposition of sodium soap.

b. improved stability and possible change in the mode of degradation.

c. binary oil system.

ponding to the complex calcium grease based on the base stock oil grade 40 and the normal calcium grease based on the spindle oil are displayed in Fig. 4 and 5.

It is clear from Fig. 1 and 2 that, with the exception of the sodium grease, the thickening agent retards the loss of the 60 LVI oil by volatilization.

Calcium stearate raises the volatilization temperature of the oil up to 237 instead of 200°C, though the concentration is in the range of 1-2%. This is related to the stability of the calcium stearate soap which starts decomposition above 340°C (Lorant 1967, Burnely and Pearson 1976). The most effective thickening agent in this group is the polymer type, which is a blend of high density polyethylene and polypropylene. This may be attributed to the tight enclosure of the oil molecules within the longer chain polymeric structure (Morway and Matuszak 1961).

The initial weight loss of the sodium grease which is based on the sodium soap of animal fats corresponds to the thermal decomposition of the soap rather than

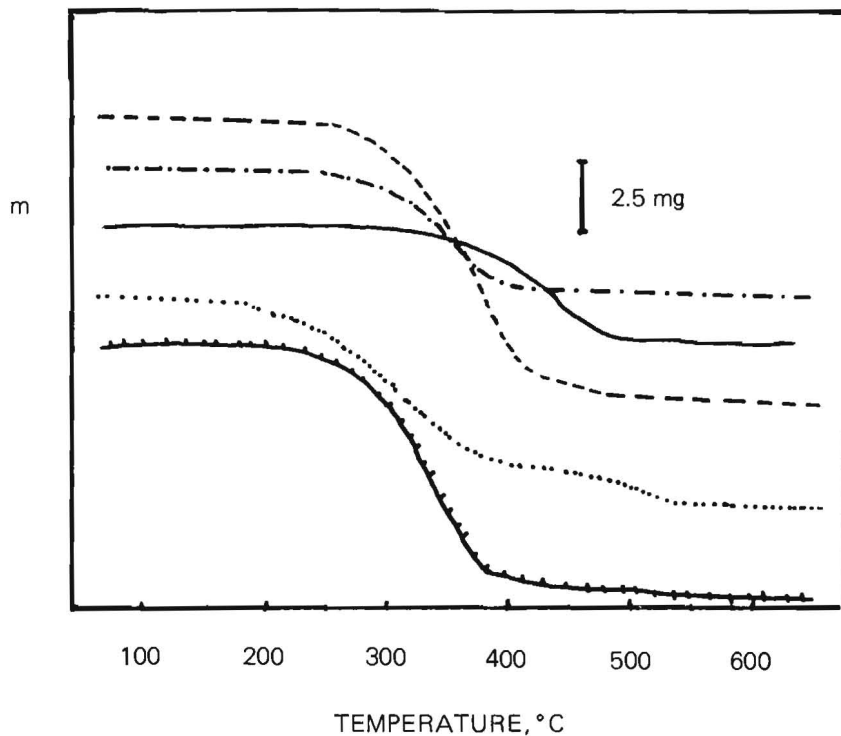


Fig. 1. Thermogravimetric curves TG of: calcium stearate greases ----, aluminium stearate grease - · - · - ·, polymer grease —, sodium base grease ·····, 60 LVI oil - · - ·.

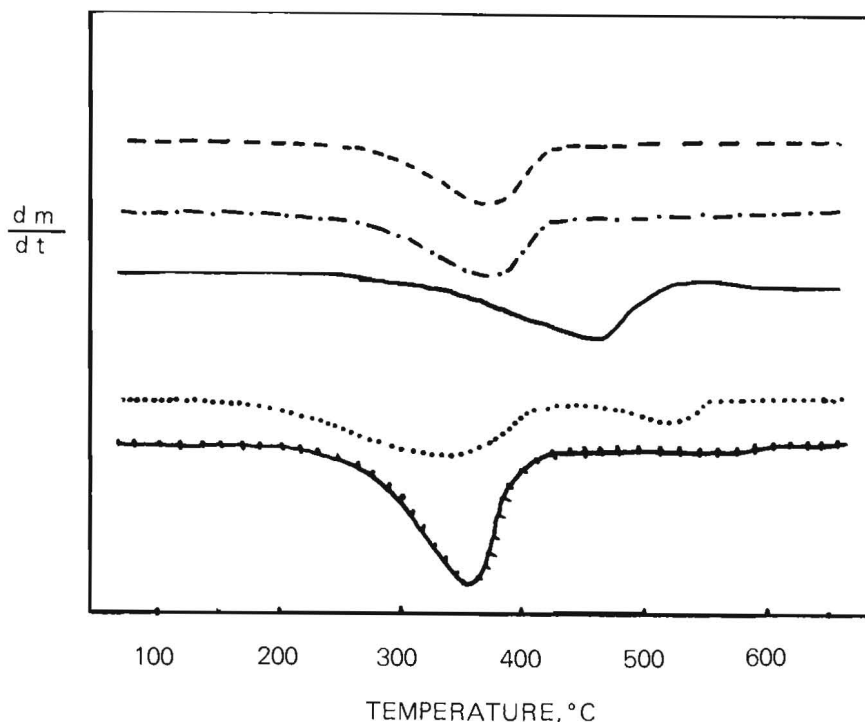


Fig. 2. Thermogravimetric curves DTG of: calcium stearate grease----, aluminium stearate grease -.-.-, polymer grease —, sodium base grease ·····, 60 LVI oil ▲▲▲▲.

the oil volatilization. This behaviour could be attributed to the splitting of the longer fatty radicals (compared to the shorter stearate radical in the calcium and aluminium greases) at elevated temperature to form shorter chain compounds.

The thermograms of the hydrocarbon grease indicated two major degradation reactions partially overlap over the temperature range involved. The complication of the thermogram is a consequence of the multicomponent nature of the grease, consisting of high molecular weight hydrocarbons dissolved in 60 HVI and grade 150 stock oils. It seems from Fig. 3 and Table 2, that the initial degradation is due to the low molecular weight hydrocarbons, although the characteristic temperatures are all in variance from the individual components.

The degradation of the complex calcium grease involves the covolatilization of more than one component as indicated on the slightly deformed DTG peak of the principal step (Fig. 4). Such behaviour is expected because of the variety of the complexing agents present in addition to the grade 40 stock oil. The thermal stabil-

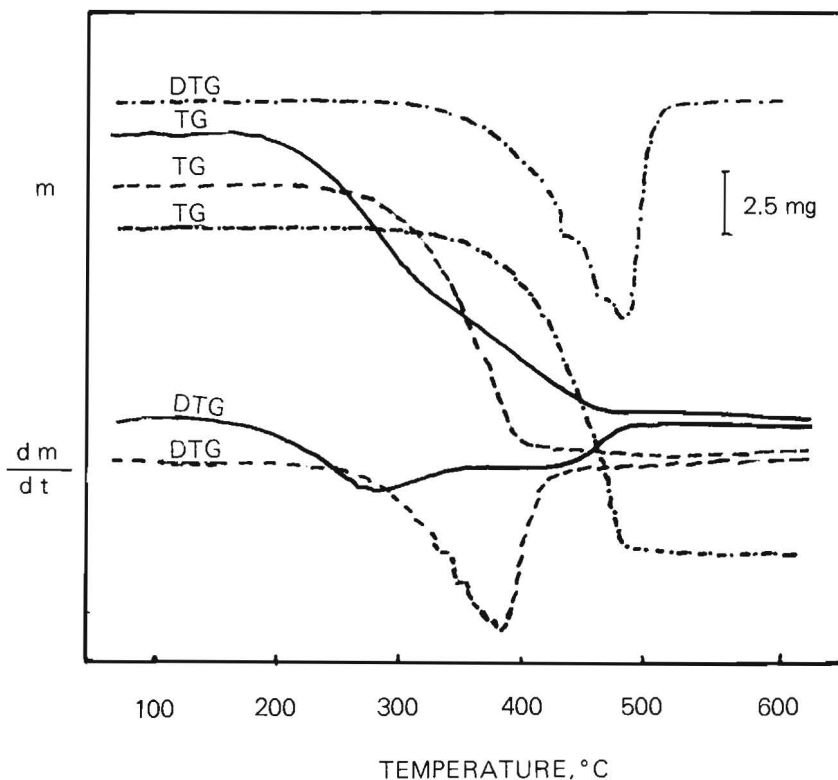


Fig. 3. Thermogravimetric curves TG and DTG of: 60 HVI oil ----, 150 stock oil - - - - - , hydrocarbon grease —.

ity of the oil is improved by 20°C using this thickening agent. The next step of the complex calcium grease decomposition is well resolved and occurs between 418-612°C involving 13.8% of weight loss from the original weight of the grease (Table 2).

Similarly the thermograms of the normal calcium grease made from the spindle oil (shown in Fig. 5) indicate the volatilization of the oil and the calcium soap by well defined steps. However, the decomposition of the soap partially overlaps with the oil volatilization leading to lower thermal stability when compared with the individual oil and slightly higher estimated concentration (*see* Table 1).

Quantitative Evaluation of TG Curves

In addition to the utility of the method in distinguishing between lubricating greases, an attempt was made to estimate the oil content of the greases on the

Table 2. Transition temperatures of the lubricating greases and oil constituents and their relative weight losses.

Grease/Oil	T ₁ °C	T _{max.}	T ₂	T ₃	T _{max.}	T ₄	%wt. loss ₁	%wt. loss ₂
Calcium stearate grease	237	372	405	—	—	—	96.6	—
Aluminium stearate grease	250	380	440	—	—	—	93.4	—
Sodium based grease	177	345	420	467	527	562	73.2	16.1
60 LVI oil	200	360	437	550	—	—	97.6	—
Polymer grease	287	466	522	—	—	—	93.7	—
60 LVI oil	200	360	437	550	—	—	97.6	—
Hydrocarbon grease	172	297	360	—	422	495	63.0	35.8
Base stock 150 oil	265	490	537	—	—	—	97.2	—
60 HVI oil	200	385	425	—	—	—	98.0	—
Complex calcium grease	177	327	382	418	515	612	76.8	13.8
Base stock 40 oil	155	275	327	—	—	—	99.24	—
Normal calcium grease	155	285	335	450	500	542	81.6	13.8
Spindle oil	162	300	332	—	—	—	99.0	—

T₁ initial temperature of first transition.

T_{max.} maximum temperature of first transition.

T₂ final temperature of first transition.

T₃ initial temperature of second transition.

T_{max.} maximum temperature of second transition.

T₄ final temperature of second transition.

%wt. loss₁ % weight loss involved in first transition.

%wt. loss₂ % weight loss involved in second transition.

basis of the TG data. In those instances, where two steps of weight loss are identified, the first step is considered as the volatilization of the oil. In others, where the thickening agent decomposes earlier than the oil, the results are at best tentative, e.g. the sodium base grease which decomposes at 177°C, i.e. 23°C lower than the 60 LVI oil. The results are reasonable with the ranges of concentrations used, as shown in Table 1. However, care must be taken with interpreting results for greases with similar behaviour but of unknown composition.

Although thermogravimetry proved to be quick and a valid method in distinguishing between lubricating greases in terms of the nature (volatility characteristics) and quantity of the base oil, it also has limitations and could be less informative, especially when studying greases composed of complex mixtures.

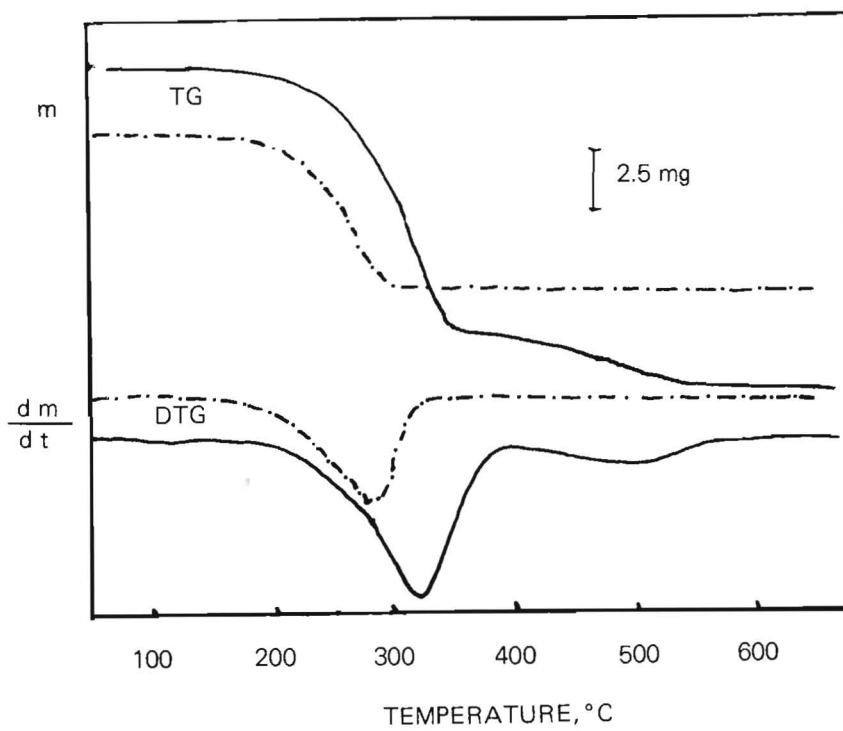


Fig. 4. Thermogravimetric curves TG and DTG of: complex calcium grease —, 40 base stock oil

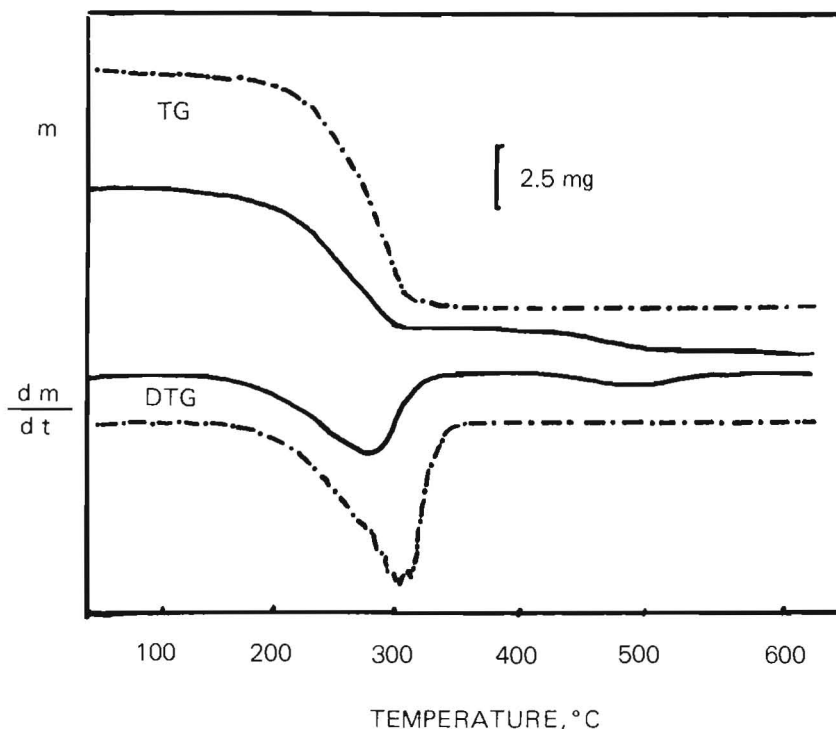


Fig. 5. Thermogravimetric curves TG and DTG of: normal calcium grease —, spindle oil - - - - -

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دراسة التحليل الحراري الوزني لشحوم التزيت

ذؤيب السامرائى و محمود بربوتى

مركز بحوث النفط - ص. ب. ١٠٠٣٩ الجادرية - بغداد - الجمهورية
العراقية .

استخدمت طريقة التحليل الحرارى الوزني فى جو نتروجيني
كطريقة منفردة فى تشخيص بعض أنواع شحوم التزيت
المحضرة .

لقد تبين أن هذه الطريقة الحرارية السريعة للتحليل
ذات فائدة كبيرة فى التمييز بين أنواع مختلفة من الشحوم
بالإضافة إلى أنها وفرت معلومات مهمة حول نوعية
المحتويات لهذه المنتجات والنسب الداخلة فى تركيبها .