Thermochimica Acta, 46 (1981) 21—45
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL ANALYSIS OF PETROLEUM PRODUCTS

MAREK WESOŁOWSKI

Institute of Chemistry and Analytics, Medical Academy, 80-416 Gdańsk (Poland)

(Received 18 November 1980)

ABSTRACT

A review is given concerning the application of thermal methods of analysis, viz. differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), derivative TG (DTG), dilatometry (DT) and penetrometry (TMA), for the investigation of petroleum products (fuel and lubricating oils, greases, paraffin waxes, petrolatums and asphalts). The presented studies include phase transitions, problems concerning the evaporation of volatile components from heavy fractions, determination of the thermal stability under atmospheric and oxygen conditions, the kinetics of these processes, as well as a study of the thermal decomposition. Particular attention is paid to works dealing with the possibility of utilization of the methods of thermal analysis for evaluation of the quality of commercial petroleum products as well as for qualitative and quantitative control of their composition. Moreover, the substitution for the rapid and fully automated methods of thermal analysis of a few expensive and time-consuming methods of classical analysis in control industrial laboratories is also pointed out.

INTRODUCTION

Petroleum, one of the most important raw materials of the chemical industry, is a mixture of paraffin, naphthenic and aromatic hydrocarbons, small quantities of oxygen-, sulphur- and nitrogen-containing compounds and ashing solids. A variety of economically important products are manufactured from them, including petrol, kerosene, fuel and lubricating oils, paraffin wax, petrolatum, asphalt and petroleum coke [1,2].

The physico-chemical properties and chemical composition of petroleum and its products can be controlled by various analytical methods. Studies carried out in recent years have shown that thermal analysis can be used as one of these methods because thermal methods of analysis such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), derivative TG (DTG), dilatometry (DT) and penetrometry (TMA) supply much information concerning petroleum products.

Because of the foregoing reasons, it has been decided in this paper to survey the application of thermal methods of analysis in the studies of the physico-chemical properties and chemical composition of petroleum products — fuel and lubricating oils, greases, paraffin waxes, petrolatums and asphalts — and utilization of the information in control industrial laboratories. With the exception of fragmentary elaborations [3—7], the problem has not previously been the subject of a review article.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

Historically, DTA is one of the oldest thermal methods of analysis. It is first of all the method of the phase analysis and for this reason reflects the changes of state occurring in the sample. The changes are only indirectly dependent on its chemical composition.

Study of oils and greases

DTA was used in the study of mineral oils from petroleums [8]. The results showed that over the range 190—370 K, the DTA curves obtained on cooling differed from those obtained upon heating of oils. The existence of very long hydrocarbon chains (which increase the molecular weight of paraffinic oils) shifts the ranges of melting and crystallization to lower temperatures. The values of heats of these two transitions (determined from the DTA peak areas) showed a similar relation. However, the heat capacity of naphthenic—aromatic oils varies with temperature to the same extent for both the solid and liquid phase of an oil. DTA has been found to be a rapid and precise method for the determination of the thermal stability of lubricating oils, petroleum and synthetic, under oxidative conditions [9]. It enables the estimation of the efficiency of additives in lubricating oils and control of the aging stability of oils during their usage.

DTA has great significance in the discussion on problems encountered in grease production. On the basis of the review of literature and the author's own works, it is suggested that DTA may be applied to the determination of the nature of phase transitions of soaps used as grease components, for the measurement of the heats of these transitions which would allow the calculation of energy balances in fat cooking processes, in establishing the model and actual phase diagrams for systems containing fats from which one could read directly the cooking temperatures of particular components, and for determination of the influence of oils and other additions on the phase diagrams of systems comprising soaps [10]. In addition, DTA can be used as a routine control technique at individual stages of grease manufacture to ensure proper thermal properties of the grease.

The DTA study of phase transitions and phase diagrams in systems containing soaps, especially those of lithium, sodium and aluminium, and a series of other grease components (liquid organic compounds, mineral oils and paraffin waxes) has been the subject of many works [11—22]. These investigations were carried out in order to bridge the gap between studies of model systems containing soaps and hydrocarbons and more complex, multicomponent systems such as soaps and thickened greases [11]. Moreover, they serve to improve the properties of greases and the formation of new compositions. DTA was also used for the estimation of the relative thermal stability of greases at ambient and elevated pressure [23] and under oxidative conditions [24], as well as in the study of the thermal decomposition of asphaltenes and tars derived from petrolatum [25].

Analysis of wax mixtures

DTA has been used to study waxes. These are mostly mixtures which may contain paraffin hydrocarbons and their derivatives, alcohols, ketones, ethers and esters, as well as aromatic compounds. Waxes melt over certain temperature ranges above 313 K, with no decomposition.

Commercial paraffin waxes are characterized by two endothermic DTA peaks due to solid—solid phase transitions and melting. The melting peak for each wax lies between the transition point and the melting point of the corresponding *n*-paraffin hydrocarbon which contains the same number of C atoms as the average number of C atoms in a given wax [26]. The transition peak is usually observed at a lower temperature than the transition point of the corresponding *n*-paraffin hydrocarbon. In addition, the transition and the melting peaks are broad as compared with those of the corresponding *n*-paraffin hydrocarbons. Based on this, the heats of fusion of waxes showed comparable values but the values of the heat of transition are smaller than those of pure *n*-paraffin hydrocarbons containing C_{24-30} atoms.

DTA studies showed that the melting points of waxes in mixtures undergo changes. A 25% content of paraffin wax in carnauba wax was found to lower its melting point by 5°, while a further increase in its content did not alter the melting point of carnauba wax beyond the difference of 6° [27]. Paraffin wax in combination with beeswax at contents lower than 50% had no effect on the melting point, but when the content of paraffin wax was 50% or more it suppressed the melting point of beeswax. Moreover, it is worth noting that small additions of carnauba wax to paraffin wax increased its melting range but beeswax did not show this effect. It was also shown that on the DTA curves of mixtures containing microcrystalline or ceresin waxes and paraffin hydrocarbons endothermic peaks characteristic of both ingredients were observed [28]. However, the plasticity limits (the lowest temperature at which the film on aluminium foil remained intact on blending) passed to a minimum at 30% content for microcrystalline wax or 15% for ceresin wax.

Based on a study of the melting and the solidification of paraffin, ester and synthetic waxes, it was concluded that over the range 293—413 K it is not yet possible to utilize the height of the DTA peak and its position on the curve for identification of different types of waxes [29]. However, by comparison of the DTA curves of mixtures of waxes with curves of particular waxes and wax-like products, it was possible to identify the components of these mixtures. In addition, accurate analysis of the shape of the DTA curves of waxes enabled a choice of the endothermic DTA peak (occurring over the range 748—754 K) to be made, which is useful in distinguishing between paraffin, microcrystalline and polyethylene waxes [30]. A relation between its area and content of waxes in the mixture can be used for estimation of these waxes in a mixture, as presented in Fig. 1. Simultaneously, the influence of the sample size, its thermal conductivity, the geometry of the crucibles, means of the sample loading in them and the heating rate on the shape of the DTA curves of waxes was also defined. Moreover, a study of montana waxes (in the crude state and after removal of resins) showed that DTA may

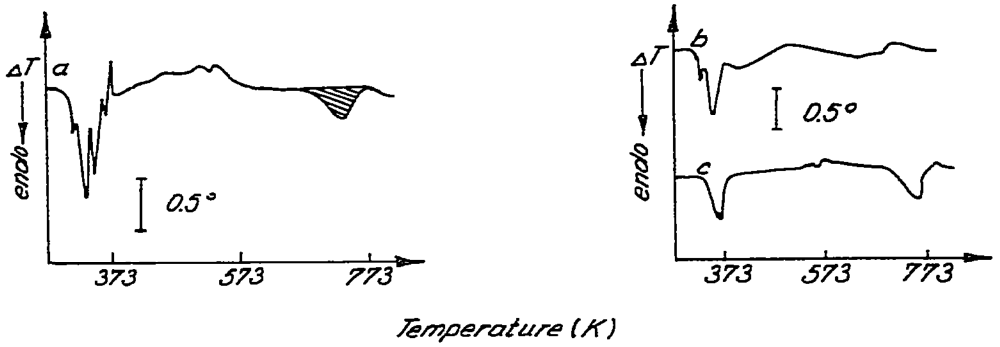

Fig. 1. DTA curves of the thermal decomposition of: a, mixture of the waxes, paraffin wax 135/140 ex and microcrystalline wax C 23 at the weight ratio 1 : 1; b, paraffin wax 135/140 ex; c, microcrystalline wax C 23 (from ref. 30). The content of microcrystalline wax in the mixture was determined based on the circumscribed area of the endothermic DTA peak.

be used as a rapid method for evaluation of their chemical composition, and especially for the determination of their resin content [31].

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

As compared with DTA, DSC has an incommensurable larger significance in the study of petroleum products. In spite of the fact that thermodynamic equilibrium is not usually achieved, DSC provides much valuable information characterizing phase transitions of samples and making possible a relatively accurate determination of a series of thermodynamic constants. Application of DSC to the study of petroleum products was previously fragmentarily elaborated in review articles [5—7].

Phase transitions in oils

A distilled lubricating oil contains about 20% wax which undergoes crystallization accompanied by phase transition [32]. The remaining wax-free part of the oil either does not crystallize or crystallizes with difficulty to form an amorphous phase associated with the glass transition. This was confirmed by measurement of the specific heat changes of distilled lubricating oil over the range 173—353 K. Two main characteristic changes are due to the glass transition and dissolution of the crystallized wax, unless the oil is completely wax free.

The temperature range of wax dissolution, 205—317 K, is dependent on the melting points and heats of fusion of the paraffin hydrocarbons contained in it. Removal of successive wax fractions lowers the upper transition temperature but not the onset temperature, which remains at 205 K. In addition, it is reflected also by a decrease in the heat of fusion of the oil. However, the values of the heat of fusion of wax fractions decrease due to the decreased *n*-paraffin hydrocarbon and increased iso-paraffin hydrocarbon contents. It is apparent from the heat of fusion values of waxes that they must be used with caution for calculation of their content in lubricating oil. Based on this information it has been shown that the shape of the DSC curves depends on the chemical composition of the distilled lubricating oil which depends on the origin of the crude oil.

The glass transition of the amorphous phase (remaining after complete removal of wax from the distilled lubricating oil) is characterized by drastic changes in the specific heat and viscosity of oil [32]. The glass transition point (T_g) (denoted as midpoint of a step on the DSC curve which corresponds to an abrupt change in the specific heat of oil vs. the temperature) is near 189 K. The T_g value does not alter due to changes in the content of wax in oil, but is affected by the chemical composition and structure of components in the amorphous phase.

An exothermic DSC peak due to the crystallization of waxes in lubricating oils occurs over a broad temperature range, 307—213 K [32,33]. The onset of this peak reflects a point where a stormy change in the properties of oil occurs, and it depends on the wax content, as shown in Fig. 2A. A comparison of its values with the cloud-point values of fuel and lubricating oils (determined by ASTM Rotary Bomb method) revealed a close linear correlation between both values. It is independent of the type and chemical composition of waxes present in the oils. A similar correlation was found between the temperatures of extreme points on the exothermic DSC peaks and the pour-point values (determined by ASTM Rotary Bomb method).

These correlations were also found during the crystallization of waxes contained in the middle fraction of a distillate from crude oil and in fuel oil for high-pressure engines, which occurred over the range 316—210 K [34]. A comparison of the characteristic temperatures is compiled in Table 1. In the case of the cloud point the linear correlation is independent of the sample weight and the presence of pour-point depressants. However, the same trend in the case of the pour point is observed only with additive-free distillates because the addition of a pour-point depressant substantially changes the

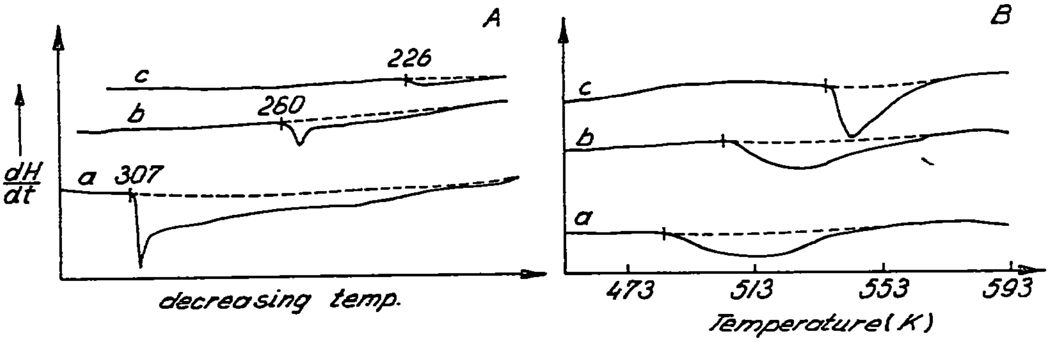

Fig. 2. DSC curves of lubricating oils (from ref. 33). A, The shifting of the onset of exothermic DSC crystallization peak due to dewaxing of lubricating oil: a = original lubricating oil, b and c = subsequent steps of dewaxing of lubricating oil. B, The effect of antioxidant on the oxidative stability of lubricating oil at 100 psi pressure: a = the onset of endothermic DSC peak due to the decomposition of original lubricating oil, b and c = lubricating oil containing 1.0%, 4.0% of antioxidant, respectively.

shape of the exothermic DSC peak (it is sharper with a steep deflection from the baseline). Moreover, this correlation also depends upon the concentration and chemical composition of wax contained in the oil, and upon the course of its crystallization on cooling.

The shape of the DSC peak due to melting or crystallization of lubricating oils is different for individual types of oils. Paraffin oils are characterized by a shallow but broad DSC peak, while naphthenic—aromatic oils show only variations in the slope from the baseline of the curve due to change in the heat capacity of the oil [35]. Examination of fractions obtained by vacuum distillation of paraffin oil showed that the extent of the crystallization and melting range decreases with increase in the average molecular weight of components of each fraction. Moreover, the temperature at the beginning of melting and the heat of melting decrease, thus indicating the suppressed paraffinic character and enhanced iso-paraffinic and naphthenic character for the subsequent fractions [35,36].

These studies showed that the information obtained by analysis of the temperature range and the shape of endo- and exothermic DSC peaks as well as the characteristic heats of transitions calculated from them, can be successfully utilized in quality evaluation of the different types of commercial oils. It was shown that in the case of using a lubricating oil of the paraffinic

TABLE 1

Comparison of the characteristic temperatures of middle distillates from crude oils containing pour-point depressants [34]

Fraction	Pour-point depressant * (%)		Cloud point (K)		Pour point (K)	
			DSC	ASTM D 2500	DSC	ASTM D 97
Escravos			259	261	256	258
433—643 K	0.07	A	258.5	261	258	249
	0.09	A	259	260	258	249
Escravos			262	263	259.5	261
458—643 K	0.02	A	261	263	260	258
	0.1	A	261		260	252
Escravos			263.5	266	262.5	264
493—643 K	0.039	A	263.5		262.5	264
	0.1	A	263.5	266	263	258
Nigerian			243	245	242	246
medium	0.1	B	242		241	
458—633 K	0.1	A	242.5		241.5	
Nigerian			247.5	250	245	249
medium	0.053	B	246.5		245.5	
458—643 K	0.053	A	248	250	247	<249
Nigerian			242.5	245	241	246
medium	0.056	C	242.5		242	
493—623 K	0.073	B	242.5	244	241.5	240

* The type of pour-point depressant is denoted as A, B and C.

type (after the course of 4000 km), in contrast to fresh oil, the crystallization range and the crystallization starting temperature were lowered [35]. However, based on the values of heat of melting of fuel oil it is possible to estimate the gas oil content (added as a fluidizing agent, reducing the paraffin wax content). In addition, the heat of melting [37] and the latent heat of the phase transition [38] of paraffin wax were used to calculate the paraffinicity of lubricating and spindle oils. Information obtained from the DSC peaks was also used in evaluation of the quality of motor oils [39], which allows the evaluation of the aging tendency of transmission and hydraulic fluids and enable the determination of the maximum temperature for their use. DSC is also a sensitive method for defining the temperature range of applicability of lubricating greases [39]. Further, based on examination of the shape of the DSC peaks of lithium stearate-based greases, an index of their hardness may be determined [40].

Stability of oils under oxidative conditions

The thermal decomposition of lubricating oils under oxidative conditions is characterized by an exothermic DSC peak over the range 483—548 K [33]. In the presence of antioxidants the onset of the DSC peak is shifted to a higher temperature and its temperature range is reduced as seen in Fig. 2B. The shift increases linearly with increasing antioxidant concentration and shows a good correlation with information obtained from the ASTM Rotary Bomb method. The possibility of using the DSC method in studying processes of thermal stability of oils under oxidative conditions and the effect of antioxidants were also reviewed in ref. 35.

The thermal decomposition of lubricating oils under oxidative conditions is a complex process, since numerous components are being oxidized at each temperature. Therefore, the value of $\mathrm{d}H/\mathrm{d}t$ is the net sum of concurrent thermal processes at a particular temperature. Assuming an overall first order process, the kinetic equation is obtained [41]

$$-\ln\frac{H_0-H}{H_0}\left(-\ln\frac{A_0-A}{A_0}\right)=kt \tag{1}$$

where H_0 is the total value of heat evolved in the reaction, H is the value of the heat evolved at time t, A_0 is the total area of the DSC peak, A is the area of the peak at time t, t is the time interval from the onset of the peak, and k is the reaction rate constant.

When $\mathrm{d}H/\mathrm{d}t$ reaches a maximum value, H approximates to 0.5 H_0, and eqn. (1) can be rewritten in the form

$$[-\ln(0.5)=kt_{1/2}=0.693]\ \frac{\mathrm{d}H}{\mathrm{d}t_{\max}} \tag{2}$$

where $t_{1/2}$ is the half-life of the oxidation at one temperature or the time interval from the onset on the DSC peak of oxidation to $\mathrm{d}H/\mathrm{d}t_{\max}$.

Both equations and that of Arrhenius were used to calculate the activation energy of the decomposition of lubricating oils under oxidative conditions, after and before reaching an extremum on the exothermic DSC peak. The results showed that the degradation energies were different for lubricating oils, depending on the boiling point and origin. When it decreases as the boiling temperature increases, it suggests that the degradation energies are related to a particular class of components whose concentration changes with increasing lubricating oil boiling temperatures.

Oxidative stability of lubricant basestock

The ability of DSC to measure directly the heat of reaction from the peak area and induction time prior to oxidation was used to define the oxidation stability of lubricant basestock [42,43]. Studies carried out in oxygen by isothermal DSC over the range 443—503 K were based on the assumption that the heat of reaction was a measure of the extent of oxidation of hydrocarbons. The lubricant basestock used was a dewaxed oil (Solvent 150 Neutral) which was separated into an aromatic fraction A, containing sulphur compounds, and a saturated fraction S. Both fractions were blended in different proportions to mimic the composition of the original oils.

These studies showed that the oxidative stability of the saturated fraction of the basestock increased with increasing content of the aromatic fraction but the optimum concentration could be determined only at 503 K [42]. The presence of polynuclear aromatic hydrocarbons and sulphur leads to an increased synergistic effect on the oxidative stability. The addition of mononuclear aromatic hydrocarbons, which include both alkylbenzenes and naphthenobenzenes, tends to decrease the stability of mixtures containing linear saturated hydrocarbons [43].

Phase transitions of waxes

Two fundamental classes of waxes are generally recognized: paraffin waxes, which are distillable and follow crystallization from the distillate as well as microcrystalline waxes, undistillable, in which microscopic crystals occur. The studies showed that the DSC curves of both classes of waxes differ [35,44]. Microcrystalline waxes begin to melt at lower temperatures and over a wide temperature range with a single broad DSC peak. This is a result of their higher molecular weight. They consist of branched and cyclic hydrocarbons as opposed to *n*-paraffin hydrocarbons which have higher melting points. However, in the case of paraffin waxes two characteristic DSC peaks are observed, one sharper due to melting and another due to the solid—solid phase transition (orthorhombic to hexagonal).

The temperature ranges of the melting and crystallization of waxes indicated by DSC are much affected by the heating rate, as shown in Table 2 [44]. A decrease in the heating rate in the case of microcrystalline waxes brings about a decrease in the endothermic DSC peak areas, accompanied by a reduction of the temperature range over which the peak occurs due to the approach of the thermodynamic solid—liquid equilibrium. The melting, crystallization and remelting curves of paraffin and microcrystalline waxes recorded at a definite heating rate were used for rapid identification of both classes of products by comparison of these curves with those corresponding to authentic waxes [45].

TABLE 2

The effect of various heating rates on melting and crystallization points of paraffin waxes [44]

Paraffin wax	Heating rate (K min^{-1})	DSC peak temperature (K)	
		M.p.	Crystallization point
Wax A	2.5	324	319.5
m.p. 319 *	5	325	317
	10	327	314.5
	20	331	310
	40	336.5	303
Wax B	2.5	326	324
m.p. 325 *	5	326.5	323
	10	328	321
	20	330	318
	40	334	313

* Melting point of paraffin wax was measured by the ASTM D 87 method (cooling curve).

Based on the DSC curves, it is possible to determine the heat of solid—solid phase transitions and the heat of melting of paraffin waxes. The determination of the latter value is particularly important for carrying out engineering calculations because it can be used together with the heat capacity to calculate the total amount of energy required to melt a given quantity of wax [44]. Moreover, a knowledge of the values of the heat of melting, those experimentally determined and theoretically calculated, makes possible the evaluation of the crystallinity of wax (content of amorphous fraction comprising frequently cyclic and iso-paraffin hydrocarbons). Calculation of the crystallinity cannot be applied to microcrystalline waxes.

The heat of melting or crystallization of paraffin waxes was used for determination of their content in bitumens (organic components of coal, soluble in the organic solvents) [46]. The obtained results differ by ±4% as compared with those obtained by conventional methods.

It has been shown that, in general, paraffin waxes had a higher total heat of transition including the solid—solid phase transition and melting than did ester waxes [47]. Variable values of the heats of transition for different batches of waxes of the same grade indicated a significant variation in their chemical composition. An analysis of the heats of solid—solid phase transitions as a function of composition of binary mixtures containing paraffin and ester waxes (carnauba or beeswax) revealed the relationship to be quadratic. This is confirmed by the dependence of the heats of transition not only on composition of the mixtures but also on the nature of the waxes. Since in an ideal mixture of waxes the expected relationship would be linear, the observed quadratic function suggested that interaction was occurring.

DSC in conjunction with gel permeation chromatography (GPC) is also a relatively rapid and inexpensive method for the quality control of paraffin waxes, especially their chemical homogeneity [48]. The melting point

TABLE 3

Comparison of the melting points from GPC and DSC measurements [48]

Sample *	Melting point (K)		ΔM.p.
	GPC **	DSC ***	
A	339.0	339.0_1	0.0
B	347.5	337.5_1	10.0
C	351.0	342.0_2	9.0
D	358.0	336.5	21.5
E	330.0	329.5	0.5
1	339.0	337.0_3	2.0
2	356.0	329.0	27.0
3	337.0	338.0	1.0
4	337.0	331.0	6.0
5	327.0	329.0_2	2.0
6	357.0	337.0	20.0

* Samples labelled A—E are the five hydrocarbon waxes for which the author needed to find replacements. Samples 1—6 are possible replacements.

** Melting point was obtained for each wax based on the carbon number of the peak in the GPC chromatogram.

*** The main factor contributing to the poorer agreement for broad distribution waxes in the presence of more than one chemical structure in these waxes, 1 = iso-paraffin, 2 = cyclic and 3 = dicyclic hydrocarbons.

profile of wax determined by use of the DSC curves and the molecular size distribution profile determined by GPC allows control of the content of paraffin waxes in elastomers, and is the basis for comparison and selection of the replacement waxes (shown in Table 3).

DSC was also used to study phase transitions due to the content of wax fraction in asphalts [49] and to investigate synthetic paraffin waxes in a series of Ruhrwaxes [50]. This method affords valuable information as to their structure, chemical composition, and solidification point, and makes possible calorimetric measurements.

THERMOGRAVIMETRY (TG) AND DERIVATIVE TG (DTG)

TG is one of the most frequently used methods of thermal analysis. Over 20% of published work includes studies carried out by this method. TG ensures a relatively direct quantitative interpretation of the results. DTG enables a more distinct discrimination of individual stages of the thermal decomposition, thus facilitating interpretation of the TG curves.

Evaporation of volatile components

In the thermal analysis of petroleum products it is important to investigate evaporation processes and distinguish them from those of thermal decomposition. Assuming the vapour of the evaporating liquid to be an ideal gas under a defined pressure, the following relationship can be used to study evaporation processes [51,52]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{MF}{\sqrt{2\pi MRT}} \cdot p_{\mathrm{g}} \tag{3}$$

where t is the time, x is the quantity of a substance evaporated up to the time t, $\mathrm{d}x/\mathrm{d}t$ is the evaporation rate, M is the molecular weight of the tested substance, F is the true surface of evaporation, R is the gas constant, T is the absolute temperature, and p_{g} is the vapour pressure.

The shape of a crucible was found to change the surface area of the evaporation during the measurements [51]. This change is further complicated by thermal dilation of the liquid and the crucible. By introducing the apparent surface of evaporation (which shows the difference between the state of the evaporated system and the liquid—vapour phase equilibrium at a given temperature) instead of the true surface of evaporation, the effect of condensation could be eliminated. The apparent surface of evaporation is only the fraction of the true surface of evaporation and depends on the temperature. The apparent surface increases with temperature for low-molecular-weight substances, changes only slightly for medium-molecular-weight substances, and decreases for high-molecular-weight substances [52]. Its dependence on the temperature is more complicated over the range higher than boiling point.

After taking into consideration that over narrow temperature ranges the dependence of the rate of evaporation on temperature can be neglected, eqn. (3) can be written in the form [51,52]

$$\log\frac{\mathrm{d}x}{\mathrm{d}t} = \log p_{\mathrm{g}} + \log c \tag{4}$$

where $c = MF'/\sqrt{2\pi MRT}$.

After transformation, with substitution of the Arrhenius equation and neglecting the temperature dependence of the heat of evaporation, the following expression was obtained

$$\log p_{\mathrm{g}} = -\frac{\lambda}{4.576T} + B \tag{5}$$

where λ is the heat of evaporation, B is the integration constant, and F' is the apparent surface of evaporation.

Combination of eqns. (4) and (5) gives the ultimate logarithmic form reflecting a direct relationship between the rate of evaporation of the liquid component and its vapour pressure

$$\log\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\lambda}{4.576T} + \log c + B = -\frac{\lambda}{4.576T} + \log C' \tag{6}$$

This equation can be used for the determination of the average heat of evaporation (this calculation does not necessitate a knowledge of the true or apparent surface of evaporation, or even that of the molecular weight of the substance).

The results of the analysis of a relationship between the rates of evaporation and temperature for water and lubricating oils showed it to be linear over the range when the apparent surface of evaporation is constant [52]. The slope of the straight line is dependent on experimental conditions.

Processes of evaporation and thermal decomposition can be distinguished with the aid of the differential kinetic eqn. (7) [51—53]. By taking a lubricating oil as a model substance it was established that up to 558 K the loss in its weight is caused by evaporation (linear relationship between the rates of evaporation and the temperatures, the rate being proportional to the surface), while at higher temperatures the loss in weight was caused by decomposition (non-linear relationship, the rate of evaporation being proportional to the loss in weight and independent of the quantity of undecomposed substance) [51]. The value of the apparent reaction order of evaporation was found to be zero when using the annular cross-section crucibles, and when use was made of the frustum of cone-shaped crucibles the apparent reaction order was in some cases negative and its definition became dubious (the logarithms of weight loss and evaporation rates are equivalent) [52].

The measurements confirmed the assumption that the kinetic theory of evaporation described by eqn. (3) may be used for consideration of the phase structure of the liquid components of petroleum products [52]. On the other hand, the composition of the gas phase modifies the temperature dependence of the rate of evaporation, independently of the evaporating substance.

In the study on the possibility of using TG and DTG in the definition of the structure of the liquid components evaporated from the mixture, the kinetic parameters were used, calculated from the following equation [54, 55]

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)(a - x)^n \tag{7}$$

where A is the pre-exponential factor, E is the apparent activation energy, a is the total weight loss after evaporation, x is the weight of substance which evaporated at temperature T, $a - x$ is the weight of the volatile component present in the crucible at temperature T, and n is the kinetic order of reaction.

The kinetic order values of the reaction and the apparent activation energies of evaporation of volatile substances (water, aromatic, alkylaromatic, paraffin and naphthenic hydrocarbons) from the mixtures with non-volatile components (*n*-paraffin hydrocarbons having an average molecular weight of 260 and residual oil) are affected by the heating rate and also by the kind of non-volatile components [54,55]. It was shown that at low temperatures the volatile substances evaporate from the mixture at a higher rate than from the pure state, in spite of the fact that the effective surface of evaporation of the mixture (practically the effective evaporation surface is only a very small fraction of the geometrical one) is obviously smaller than that of the pure liquid. It is concluded that the non-volatile components act as an accelerator to the evaporation process. This indicates the importance of the structure of the liquid for the evaporation process. When the concentra-

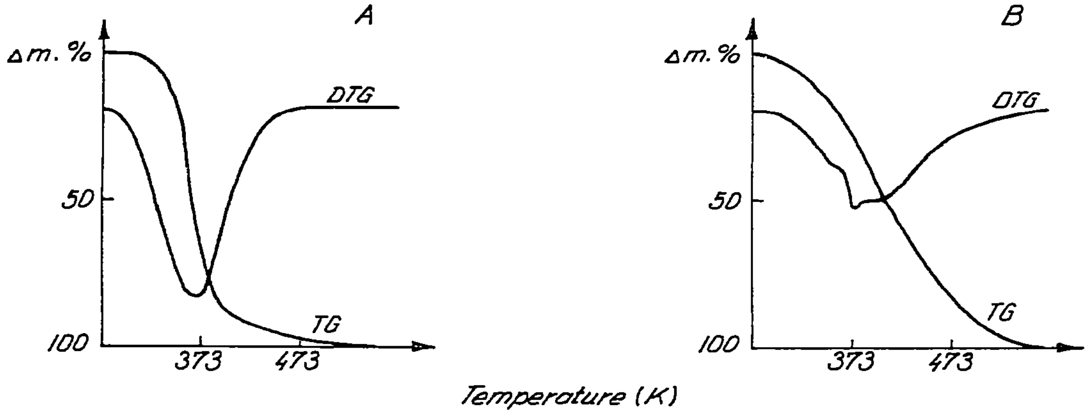

Fig. 3. TG and DTG curves of the evaporation of a compound from the mixtures containing benzene (Bz) and residual oil (Ro) (from ref. 55). A, The evaporation curves of a mixture of 69% Bz and 31% Ro; B, the evaporation curves of a mixture of 7% Bz and 93% Ro.

tion of the volatile substance in the mixture decreases, the value of the activation energy is seen to decrease, the DTG peak extremum to slightly increase up to the higher temperature, and the temperature range of the process of evaporation to extend especially because the high temperature limit is shifted up. The presence of non-volatile components is reflected by a change in the shape of the TG and DTG curves, the multiplicity of the DTG peaks is shown in the place of one single peak (reflected in Fig. 3).

The observed effect of the non-volatile components on the evaporation kinetics is tentatively explained by assuming that molecules of the non-volatile component are resolved by the volatile molecules at high concentrations, thus preventing the formation of the liquid structure [44,45]. At low concentrations of the volatile substance the dissolution becomes incomplete and a structure of the non-volatile component is formed through which the volatile molecules must diffuse on the surface and then evaporate. This liquid structure is reflected by the multiplicity of the DTG peaks.

The diffusion constant of the volatile substance from the non-volatile matrix should be important in determining the evaporation kinetics. The temperature dependence of the diffusion constants of volatile substances in mixtures with *n*-paraffin hydrocarbons or residue oil shows a significant difference which depends on the kind of non-volatile components [54,55].

Thermal decomposition of oils

Based on the TG study of crude oils, it was shown that no correlation exists between the thermal stability of oils and their density, viscosity and chemical composition [56]. By comparing the TG curves of decomposition of crude oils under an atmosphere of air and the curves of their evaporation under an atmosphere of nitrogen, crude oils can be grouped into three types: type I is when there is a large relative weight gain of crude oil starting at about 477 K but at about 588 K there is a sudden and very rapid oxidation;

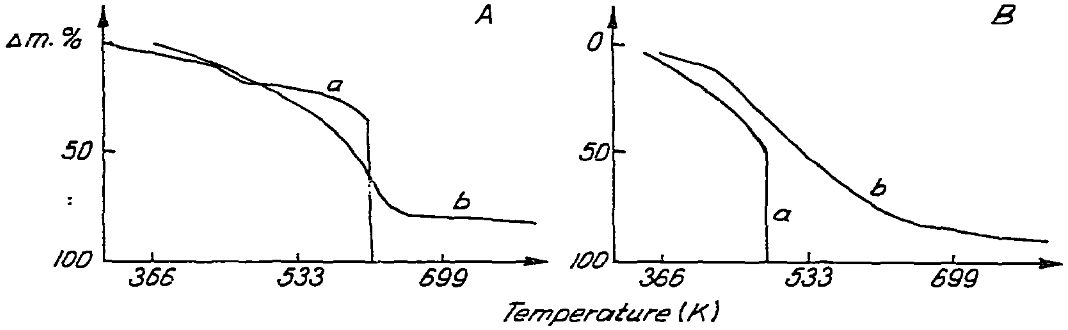

Fig. 4. Typical TG curves of the thermal decomposition of crude oils registered under atmospheres of air (a) and nitrógen (b) at 1000 psi pressure (from ref. 56). A, Type I: crude oil from the Mississippi source; B, type II: crude oil from the African source.

in type II the loss in weight occurs almost immediately after heating and there is a very rapid oxidation at about 477 K (these are shown in Fig. 4); type III show a rather gradual change, the oxidation TG curves closely parallel the nitrogen curves.

All types of oils are completely oxidized over the range 644—699 K, depending on the oxygen partial pressure. Based on these data it was shown that the dependence of the performance of crude oils on the temperature and pressure is changed in a different way for different oils and can easily be determined using thermal methods of analysis. The weight gain at both low and high temperatures for types I and III crude oils shows that the use of oxygen at low temperatures changes drastically the quality and quantity of crude oil.

The usefulness of TG as an industrial method for the control of chemical composition of crude oils was presented in ref. 57. Particularly stressed was the possibility of microdistillation of crude oils and the determination of the content of asphalts in them. DTA is useless in showing either process.

A study of the thermal decomposition of motor oils (containing only refined oil and a variety of additives), performed over the range 293—1273 K, showed that each oil has been characterized by definite distributions of the weight losses and temperature above which no further changes occurred in the sample [58]. In contrast to the atmosphere of nitrogen, the atmosphere of oxygen accelerated the thermal decomposition of oil, and shifted its maximum loss in weight to lower temperatures. The TG and DTG curves (expressed as a percentage loss in weight recorded for 25 or 50° temperature intervals) are relatively clear and sufficiently characteristic for distinguishing individual oils. Analysis of fuel oils of various origin showed that the lignite—tar-based oils proved to have relatively stable composition (total losses in weight were 96.4—97.8%); on the contrary, petroleum-based oils showed considerable variations in composition (in relation to the origin of petroleum, total losses in weight were 92.2—99.6%) [59].

Based on the thermal decomposition of fuel oils and heavy tar fractions from petroleum and brown coal, it is also possible to determine the content of a fraction decomposed above 773 K [59—61]. This fraction consists of asphaltenes (undistillable fractions of petroleum with condensed polycyclic structures and the highest molecular weight, C : H ratio and sulphur content). These fractions are undesirable constituents of fuel oils on account of their considerably longer time of thermal decomposition and far higher coke residue. Under the operating conditions, asphaltenes have a tendency to form a solid residue in the reservoirs, and to cause stoppage of pipelines and nozzles.

The measurements also showed the usefulness of TG and DTG as a very prompt analytical method enabling technological evaluation of chemical composition and properties of fuel and lubricating oils as well as asphalts [59,60,62] and heavy tars fractions from petroleum and brown coal [61]. Results obtained by this method are dependent on experimental conditions, e.g., an increase in the heating rate retarded thermal decomposition of the sample but an increase in the quantity of purged gas (air especially) significantly accelerated gasification and displaced the maximum weight losses to lower temperatures. By changes in the heating rate as well as the kind and quantity of purged gas, the laboratory conditions can be adapted to the operational conditions, thus increasing their practical significance.

Complicated chemical composition and heat transformations occurring under an atmosphere of air made classical interpretation of the results of the thermal decomposition of lubricating oils difficult [63]. Based on analysis of the shape of the TG curve (and simultaneously the DTG and DTA curves) the characteristic parameters for oils can be indicated, such as T_s as the temperature of the fractional stability of oil and t_s as the time for its reaching stability (over the range due this stage, no irreversible physical change and chemical reaction occur in the oil); T_p as the temperature of the chemical stability of oil, t_p as the time for its reaching stability and m_p as the weight of evaporated fraction (this stage quantitatively described the evaporation of the most volatile fractions of heated oil); T_k as the temperature of the heat aging of an oil, t_k as the time for its reaching it and m_k as the weight loss of heated oil due to its heat aging (an exothermic DTA peak due to this stage reflected the value of energy evolved in the time of total exothermic reactions of the heat aging of oil. The ultimate completion of this stage occurs at the extreme point on the DTG peak); T_{gr} as the temperature of the coking heat of oil, t_{gr} as the time for reaching it and m_{gr} as the weight loss of sample due to this stage (in this temperature range the coking heat of oil is observed. The weight of coke can be determined from the TG curve. The end of this stage takes place at the onset of the endothermic DTA peak due to coke decomposition).

The presented characteristic parameters for lubricating oils may be a measure of their exploitation utility [63]. The parameters can be used in works in which new lubricating oils are compounded and for the evaluation of the usefulness and influence of additives on their properties. Moreover, they enable the analysis of the course of tribological aging of the working oil as well as to foresee the time of its effective work.

The possibility of quantitative interpretation of the TG curve enables its use in the long-term volatility studies of greases. The volatility was predicted based on the parameters W_{10}, which may be marked even 10% loss in weight on the TG curve and is defined as significant volatility, and the temperature at which this loss in weight occurs, which is called the critical temperature (T_{10}) [64]. The W_{10} value was found by averaging the data from several oils and greases, and had the value 4%. Further, the temperature for starting of long-term volatility testing could be determined from the 4% loss line on the TG thermogram by noting the temperature at which this line intersects the TG curve.

TG was used in the study of the thermal stability of lubricants under oxidative conditions [65—68]. The results showed that the stability of lubricants (oils MS-20, SU and C-220 used with calcium soap in the thickened form) depends on their chemical composition and significantly increases with the increase of the C aromatic content in the distillate fraction [65]. At 373 K under atmospheres of air and nitrogen an endothermic effect apparently due to the elimination of water is shown on their thermograms [66, 67]. However, other endothermic effects over the ranges 593—623 K and 723 K were due to the destruction of calcium soaps and boiling of the dispersion media of greases in an atmosphere of air at above 473 and 573 K, respectively. In contrast to SU oils, the higher stability of lubricants based on MS-20 oils resulted from the presence of more tertiary C atoms and heavy alkylcycloalkanes.

Isothermal TG has also been used for studying of the thermal and thermooxidative stability of polyvinyl chloride—lubricant systems (polyvinyl chloride plays an outstanding role in the plastic industry and its processing requires a variety of auxiliary materials, out of which lubricants are very important) [69]. The studies showed that the addition of Stenol PC and lead stearate lubricants increased the stability of polyvinyl chloride if used at 3—5% and 1—2% concentration, respectively. The stability of polyvinyl chloride decreased with increasing stearic acid at 1—3% concentration.

Quantitative analysis of wax mixtures

TG was used in the semi-quantitative determination of the composition of wax mixtures. Analysis of the shape of the TG curves of mixtures containing paraffin wax and the components of dental inlay waxes, carnauba and beeswax showed that the intersection of the straight lines obtained by extrapolating the slopes of the TG curves above and below an inflection temperature allowed the determination of the weight loss and thus the percentage of the components [70]. A dependence of the shape of the TG curves on the content of the waxes in the mixture is shown in Fig. 5A. The results of semiquantitative determinations were relatively good for carnauba wax and beeswax over the concentration ranges 2.5—75.0% and 2.5—50.0%, respectively. It must be noted that the determinations were more possible for mixtures having components with much differentiated melting and boiling points.

Quantitative calculations of the composition of paraffin wax mixtures were also facilitated by the fact that over the range of the highest loss in weight the thermal decomposition curves of the waxes were almost rectilinear [71]. Under the condition that the thermal decomposition of two pure waxes differs by at least 20°, it is possible, based on a knowledge of the

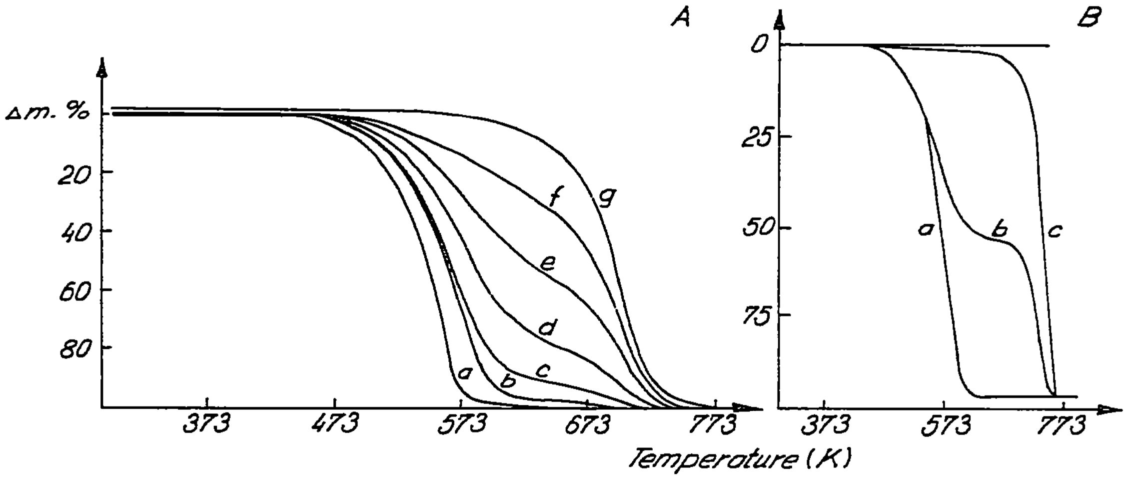

Fig. 5. TG curves of the thermal decomposition of mixtures of two waxes based on whose shape the content of one of the waxes was determined. A, Mixtures of paraffin wax (Pa) and carnauba wax (Ca): a = 100% Pa, b = 97.5% Pa and 2.5% Ca, c = 90% Pa and 10% Ca, d = 75% Pa and 25% Ca, e = 50% Pa and 50% Ca, f = 25% Pa and 75% Ca, g = 100% Ca (from ref. 70). B, Mixtures of paraffin wax (Pa) and polyethylene wax (Pe): a = 100% Pa, b = 50% Pa and 50% Pe, c = 100% Pe (from ref. 71).

shape of their TG decomposition curves, to determine the percentage content of one of them in the mixture by the following equation

$$K_2 = a + \frac{ab}{c} \tag{8}$$

where a is the percentage weight loss of the mixture between T_1 and T_2, b is the percentage weight loss of the pure component K_2 up to T_1, c is the percentage weight loss of the pure component K_2 over the range T_1—T_2, and T_1 and T_2 are the temperatures of the thermal decomposition of the components K_1 and K_2, T_2 being greater than T_1.

A graphical method of measuring the a, b and c values is shown in Fig. 5B. The content of polyethylene paraffins over the concentration ranges 15—95% and 10—85% in the mixtures with paraffin and microcrystalline waxes determined by this method were in satisfactory agreement with declared compositions of the mixtures.

TG also enables the determination of the approximate percentage distribution of low- and high-molecular-weight fractions of some paraffin waxes. The distribution of the molecular weight of wax is reflected by the slope of the TG curve, shown as a function of temperature [70]. The TG curve flattens as it increases. The temperature at the point of intersection of the straight line, obtained by extrapolation of a rectilineal sector of the TG curve with the line due to zero loss in weight, corresponds to a definite molecular weight [71]. This relation can be used for the determination of molecular weights of paraffin waxes under the condition that they do not exceed a value of 1200.

Thermal decomposition of higher fractions of petroleum

The purpose of some studies was also the thermal decomposition of asphaltenes and maltenes [72]. Based on the measurements performed under an atmosphere of nitrogen with isothermal TG at 483 and 673 K and gas chromatography, it was shown that the major volatile products of decomposition of asphaltenes and maltenes are aliphatic C_1—C_7 hydrocarbons, CO, CO_2, COS and H_2S, and that the distribution pattern of these products is very similar in both cases, as shown in Table 4. It was also shown that the thermal decomposition of asphaltenes and maltenes at 673 K becomes much faster than at 483 K, although according to the TG curves taken over the range 298—1273 K the decomposition rate at this temperature is rather slow.

TG is also useful in discriminating between samples of crude petroleum from the Alaskan field and those from fields in other regions of the world. The TG curves of petroleum are characterized by three stages of thermal decomposition: evolution of a light volatile fraction, a heavy non-volatile fraction and formation of a coke residue and ash [73]. Their quantitative interpretation has led to the designation of three fundamental criteria for discrimination between petroleum samples: the graphic overlapping of the investigated TG curves with those from the Alaskan field; the ratio of weight loss of the light volatile fraction to the residual carbon and ash content which for petroleum from the Alaskan field is less than 22; and the percen-

TABLE 4

Chemical composition of the volatile components of the thermal decomposition of asphaltene and maltene from the Athabasca oil sand [72]

Volatile components of decomposition	Asphaltene *		Maltene *	
	483 K	673 K	483 K	673 K
Methane	54.3	209 000	16.7	142 000
Ethylene	0.76	8770	0.29	5700
Ethane	0.76	95 500	0.25	62 200
Propylene	2.80	22 100	0.29	20 600
Propane	2.60	63 000	0.29	69 700
Isobutene	0.56	6750	0.44	17 600
Butane	0.84	19 200	0.25	19 300
Butenes	<0.1	47 500	<0.1	51 700
Pentanes and pentenes	n.d.	46 500	n.d.	61 500
C_6	n.d.	45 700	n.d.	73 700
C_7	n.d.	29 000	n.d.	57 500
Carbon monoxide	484.0	9410	53.5	11 800
Carbon dioxide	197.0	5000	150.0	4500
Carbonyl sulphide	1.64	210.0	0.40	112.0
Hydrogen sulphide	<8.80	<89 500	<1.93	<56 000

* 1 kg of oil sand used in these experiments contained 28 g asphaltene and 138 g maltene. Each sample was heated at a given temperature for 20 h. The concentration was 10^{-8} mole kg^{-1} of oil sand.

n.d. = Not determined.

tage weight loss of the heavy non-volatile fraction which should lie within the range 23.5—31.5%.

This is a valuable and rapid method (the total time required for measuring being 14 min per run up to 1023 K at a special temperature programme), there was no special sample preparation (other than agitation of the bulk sample and no extensive clean-up afterwards). To record one thermogram a sample size of 10 mg is required (does not require large bulk samples). Moreover, TG eliminated most of the potential environmental pollution associated with other methods of analysis.

DILATOMETRY (DT) AND PENETROMETRY (TMA)

DT and TMA indicate the occurrence of definite physical changes in a sample but do not give direct information as to their character. They are most frequently used in the study of first order phase transitions, and are relatively seldom used in thermal analysis.

Measurements by DT of the phase transitions in solid paraffin hydrocarbons from narrow cuts of raffinate oils and slack wax as well as commercial paraffin and ceresin waxes (ceresin wax is a purified soil wax) showed that the temperature range of the solid—solid phase transitions widened with increasing difference between the melting points of the hydrocarbons present in the sample [74]. However, the temperature interval between the phase transition and the melting point diminished linearly with increasing melting point. The DT has been shown to be a suitable method for the evaluation of performance characteristics of paraffin and ceresin waxes. The usefulness of DT was also proven based on structural investigations, evaluation of chemical composition, and characterization of the melting and the solidification processes of synthetic paraffin waxes in a series of Ruhrwaxes [50].

Results of TMA and DTA of paraffin, ester and synthetic waxes showed that the resistance to penetration of waxes is closely related to the presence of the solid—solid phase transition and melting, over the temperature range in which these transitions occur [75,76]. Moreover, experimentally the penetration is dependent on such factors as the time, temperature, load and the heating rate, as reflected in Fig. 6.

It was demonstrated that paraffin waxes exhibit a poor resistance to penetration at the temperatures corresponding to the solid—solid phase transitions, but the melting temperature has little effect on penetration. Therefore, the melting temperature may provide a poor criterion in the selection of paraffin waxes used in the formulation of dental inlay waxes [75]. The melting temperature is important, however, as a criterion in the selection of hard ester waxes.

The presence of the solid—solid phase transitions and melting of lower components has comparatively little effect on the resistance of these ester waxes to penetration. For this reason some of them (carnauba and beeswax) are frequently added in small amounts to paraffin wax because a pronounced effect on increasing penetration resistance is observed.

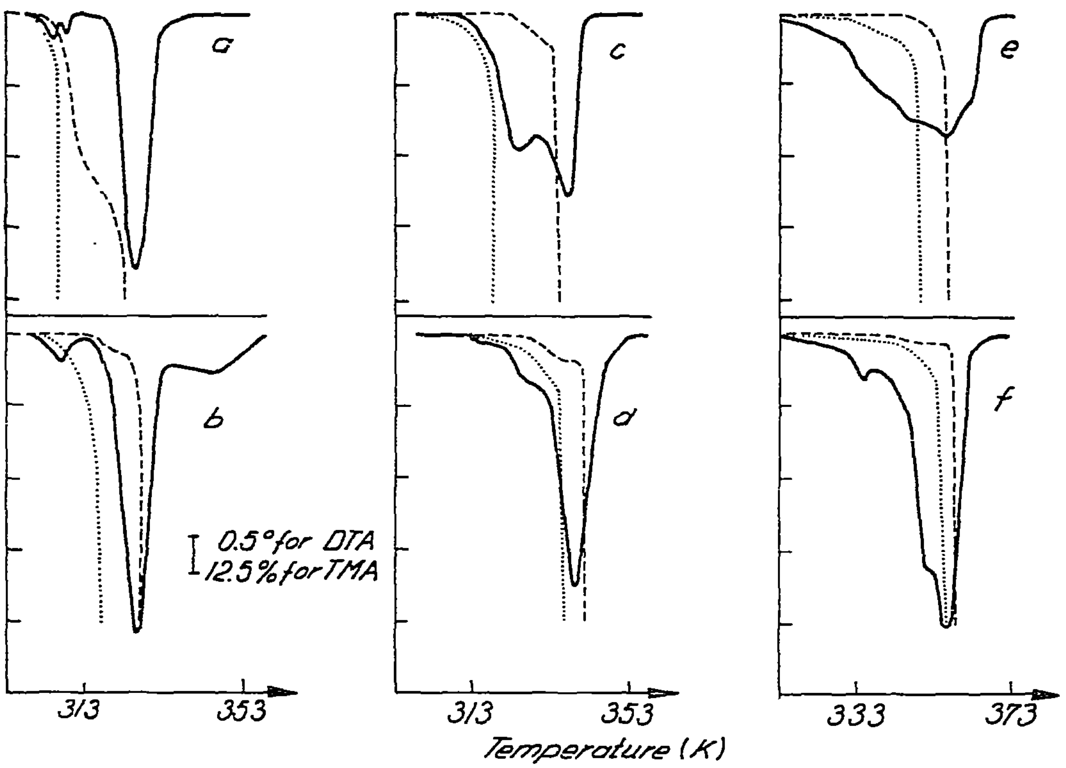

Fig. 6 . DTA curves (———) and TMA curves under loading 1.25 g mm^{-2} (- - - - - -) and 25.5 g mm^{-2} (· · · · · ·) for hydrocarbon waxes: a = paraffin wax, b = ceresin wax, and for ester waxes: c = beeswax, d = candelilla wax, e = montana wax, f = carnauba wax (from ref. 75).

An analysis of the relation between the solid—solid phase transitions and the penetration temperature at a stress level of 250 kPa showed that a linear correlation exists for paraffin waxes [76]. Penetration of the mixtures of waxes containing both paraffin and ester components was determined by melting the paraffin waxes. This was revealed by analysis of commercial dental impression waxes.

SIMULTANEOUS THERMAL METHODS OF ANALYSIS

Simultaneous utilization of the thermal methods of analysis proved to be more advantageous because results obtained by the particular methods facilitate their mutual interpretation. At present, simultaneous recording of the DTA and TG curves is more frequently performed. DTA allows one to show whether the studied conversion is accompanied by an endo- or exothermic effect and, with the aid of suitable systems, one can measure its value. However, based on TG and DTG, accurate values of changes in weight of the sample can be determined and used in the form of chemical reaction in accordance with which the thermal decomposition occurred.

The most frequently used instrument enabling simultaneous recording of

DTA, TG and DTG curves is the derivatograph. Reviews on the possibilities of its utilization in the studies of petroleum products can be found in several papers. The derivatograph can be used for recording approximate distillation curves, cracking distillation curves, for determination of temperature ranges of the first order phase transitions, and for studying the thermal stability under air or oxidative conditions of crude petrochemicals and their products. The presented possibilities are confirmed by examples of the study of thermal decomposition of industrial oils [77—79], paraffin and ceresin waxes, as well as distillation of gasoline and gas oil [78].

The derivatograph enables distinct separation on a thermogram of products of thermal pyrolysis of mineral oils, evaporated portions of an oil part and residued resinous material [80], as well as facilitating the identification of distilled and residual components of fuel oils [81]. Moreover, based on the data presented, it was shown that the derivatograph can be used in laboratory tests for the quality control of commercial lubricating oils, since the boiling ranges, the thermal decomposition temperatures and the coking points can easily be determined [82]. In the case of analysis of high-boiling lubricating oils the results are poorer than those obtained by the vacuum-distillation method.

The derivatograph was used in the studies of greases. The temperature ranges of melting, evaporation of water and thermal decomposition of plastic lubricants can be determined with some precision [83]. Moreover, the derivatograph is able to define the drop point and determine phase diagrams for systems containing lubricating components [84], and may be applied to the study of the thermal decomposition of mixtures comprising lubricating components [85]. This has been confirmed by a study of thermal decomposition which showed that the sodium-based lubricating greases, in contrast to calcium-based lubricating greases, lost water at lower temperatures than the pour points, thus indicating that the fluidity of calcium-based lubricating greases is due to decomposition of a calcium soap—water complex [86,87]. The derivatograph is also applied in the determination of the evaporation ranges of light oils used as diluents for lubricating greases, the phase transition temperatures of soaps containing about 20% of lubricating greases, and the thermal decomposition of unsaturated fatty acids contained in lubricating greases [87].

The existence of a direct relation between the phase transition temperatures of plastic lubricants and their behaviour in the mobile conditions makes possible the use of the derivatograph as a rapid instrument for predicting the performance of plastic lubricants [88]. Moreover, thermal analysis of calcium-based lubricating greases, all of the components of these greases and their mixtures, showed that the derivatograph can afford relatively quick information on the chemical composition and expected behaviour of the tested lubricating greases and that these allow, in some instances, a better evaluation of the results than conventional analytical data [89].

The derivatograph can also afford substantial information as to the choice of petroleum base raw materials, destined for coke production (about the quantities of coke preparation) [90]. It was shown that thermal analysis does not provide an exact repetition of the coking process because it occurs at other physical parameters, e.g., under these conditions the processes of evolution of the volatile decomposition products proceed relatively easily, whereas the processes of condensation and polymerization occur reluctantly. Thermal analysis affords all the information about the temperature ranges and the directions of courses of reactions due to heating. This is also confirmed by the study of thermal decomposition of asphaltenes [91, 92]. The simultaneous determinations of the volume of the evolved volatile products showed that over the range 573—673 K the cleavage of weak chemical bonds took place, whereas above 673 K thermal degradation of the asphaltene structure occurred.

The derivatograph was used for investigation of the kinetics of thermal decomposition of a residue remaining after vacuum-distillation of crude oils [93]. The investigations carried out under isothermal conditions showed that the kinetics of more complicated chemical reactions of decomposition (in which the reaction rate is not constant but depends on the extent of reaction) are best described by the general relationship [93]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k^p \alpha \,(1-\alpha)^q \,, \qquad \text{or} \qquad \frac{\mathrm{d}\alpha}{\alpha^p(1-\alpha)^q} = k\,\mathrm{d}t \tag{9}$$

where α is the extent of reaction (the mole fraction of decomposed sample), p and q are the homogeneity factors.

Good results such as those obtained for decomposition at lower temperatures (573, 623 and 673 K) were not obtained at higher temperatures (723 and 773 K). At these temperatures the process occurs very quickly and is more complicated.

Studies of petroleum products performed by the derivatograph have also been described in previous works [51—55,63,65—67,69], similarly as a study of the thermal decomposition of crude oils performed by simultaneous DTA and TG, and with instruments other than the derivatograph [56,57]. Attention should also be paid to the studies of the simultaneous use of DTA, TG and DTG techniques for batch-control of synthetic lubricants [94]. The studies were supplemented by investigation of residues obtained during complete or partial thermal decomposition of lubricants with IR spectroscopy, and analysis of volatile reaction products with gas chromatography and mass spectrometry . Moreover, DTA was also used simultaneously with TMA in the study of the phase transitions of waxes [75,76] and with IR spectroscopy in the study of heating and cooling processes of mixtures of lubricating grease components [18] and of the phase transitions of soaps [19—21], with dielectric measurements in the study of soap [14,17], DSC with GPC in the study of chemical homogeneity of waxes [48], whereas TG was used simultaneously with IR spectroscopy in the study of the thermal stability of lubricating oils [65—67], with conductometry in the study of thermal stability in oxidative conditions of polyvinyl chloride—lubricant systems [69], and with gas chromatography in the study of volatile products of decomposition of asphaltenes and maltenes [72]. Simultaneous use of the several methods enables a more complete interpretation of the results.

Finally, it should be mentioned that the several original instruments for thermal analysis, DTA [18,29,95,96], DSC [40,97] and TG [98,99], were described, their use in the investigation of petroleum products being proved by the authors.

REFERENCES

1 Encyklopedia Techniki, Chemia (Technical Encyclopaedia, Chemistry), WNT, Warsaw, 3rd edn., 1972.
2 D.A. Shirley, Chemia Organiczna (Organic Chemistry), WNT, Warsaw, 1968, p. 172 (translation from English).
3 G. Kalmutchi, Rev. Chim. (Bucharest), 27 (1976) 67.
4 N.A. Nechitailo, Neftekhimiya, 18 (1978) 827.
5 F. Pochetti, Riv. Combust., 25 (1971) 461.
6 F. Pelizza, Riv. Combust., 26 (1972) 279.
7 C. Giavarini, Rass. Chim., 24 (1972) 161.
8 C. Savu, F. Pochetti and C. Giavarini, Pet. Gaz., 20 (1969) 521.
9 A. Commichau, Erdoel Kohle, Erdgas, Petrochem., 25 (1972) 322.
10 N. Trzebowski, Freiberg. Forschungsh. A, 367 (1965) 257.
11 D.B. Cox, J. Phys. Chem., 62 (1958) 1254.
12 H. Wochnowski and R. Freitag, Schmiertech. Tribol., 24 (1977) 69.
13 N.K. Volobuev, A.V. Zubkevich, O.V. Ataeva, S.I. Krakhmalev and I.V. Pavlov, Tr. Vses. Nauchno-Issled Inst. Pererab. Nefti, 16 (1976) 85 (from Ref. Zh., Khim., (1977) Abstr. No. 11 P287).
14 I.G. Fuks, V.V. Perekrestova, O.E. Gar and E.M. Uvarova, Neftepererab. Neftekhim. (Moscow), 7 (1975) 18.
15 I.G. Fuks, N.K. Man'kovskaya, Yu.L. Ishchuk, O.E. Gar, T.V. Fedorova and I.A. Lifanova, Tr. Vses. Ob'edin. Neftekhim., 11 (1976) 17 (from Ref. Zh., Khim., (1977) Abstr. No. 9 P321).
16 V.A. Dagaev, Z.I. Buyanova and Yu.V. Tanchuk, Plast. Smazki (Kiev), (1975) 137 (from Ref. Zh., Khim., (1975) Abstr. No22 P277).
17 Z.I. Buyanova, L.V. Podlinnykh and V.A. Dagaev, Neftepererab. Neftekhim. (Kiev), 15 (1977) 6.
18 O. Henning and N. Trzebowski, Freiberg. Forschungsh. A, 164 (1960) 293.
19 V.A. Dagaev, V.I. Lozovaya and N.K. Man'kovskaya, Kolloidn. Zh., 38 (1976) 148.
20 V.I. Lozovaya, V.A. Dagaev, T.V. Medvedeva, N.K. Man'kovskaya and A.P. Maksimilian, Zh. Prikl. Khim. (Leningrad), 51 (1978) 1614.
21 H. Dunken, H. Winter, E. Boeck and N. Trzebowski, Schmierst. Schmierungstech., 29 (1968) 27.
22 Z.I. Buyanova, V.A. Dagaev, A.K. Maskaev and Yu.V. Tanchuk, Zh. Prikl. Khim. (Leningrad), 50 (1977) 1353.
23 A.A. Krawetz and Th. Tovrog, Ind. Eng. Chem., Prod. Res. Dev., 5 (1966) 191.
24 R.D. Novoded and M.V. Bogdanov, Plast. Smazki (Kiev) (1975) 153 (from Ref. Zh., Khim., (1975) Abstr. No. 24 P306).
25 I.A. Posadov, N.V. Sirotinkin and Yu.V. Pokonova, Issled. Obl. Khim. Tekhnol. Prod. Pereab. Goryuchikh Iskopaemykh., (1975) 4 (from Ref. Zh., Khim., (1976) Abstr. No. 12 P277).
26 Sh. Kawasaki, H. Komizu and T. Uchida, Kogyo Kagaku Zasshi, 69 (1966) 1315.
27 R.G. Craig, J.M. Powers and F.A. Peyton, J. Dent. Res., 46 (1967) 1090.
28 I.G. Anisimov, M.G. Mitrofanov and A.V. Melikhova, in M.G. Mitrofanov (Ed.), Proizvodstvo i Primenenie Neftyanoj Tserezinov i Voskov, Nizhne-Volzh. Knizhnoe Izd., Volgograd, 1970, p. 44.
29 J. Lange and H. Jochinke, Fette, Seifen, Anstrichm., 67 (1965) 89.
30 B.R. Currell and B. Robinson, Talanta, 14 (1967) 421.
31 S.E. Severinovskii, N.N. Umnik, V.P. Ul'yanov, L.N. Menzhulina and Ya.I. Makarovskii, Khim. Tverd. Topl., 1 (1975) 134.
32 F. Noel, Thermochim. Acta, 4 (1972) 377.

33 F. Noel, J. Inst. Pet., London, 57 (1971) 354.
34 F. Casellato, C. Vecchi and A. Girelli, Riv. Combust., 27 (1973) 125.
35 C. Giavarini and F. Pochetti, J. Therm. Anal., 5 (1973) 83.
36 C. Giavarini, F. Pochetti and C. Savu, Riv. Combust., 23 (1969) 448.
37 C. Giavarini, F. Pochetti and C. Savu, Riv. Combust., 23 (1969) 496.
38 C. Savu, C. Giavarini and F. Pochetti, Pet. Gaz., 21 (1970) 117.
39 C. Lovász, Erdoel Kohle, Erdgas, Petrochem., 30 (1977) 219.
40 M.J. Vold, Y. Uzu and R.F. Bils, NLGI Spokesman, 32 (1969) 362.
41 F. Noel and G.E. Cranton, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 3, Plenum Press, New York, 1974, p. 305.
42 G.E. Cranton and F. Noel, J. Inst. Petrol. (Tech. Pap.), IP 74-005, 1974.
43 G.E. Cranton, Thermochim. Acta, 14 (1976) 201.
44 H.R. Faust, Thermochim. Acta, 26 (1978) 383.
45 B. Flaherty, J. Appl. Chem. Biotechnol., 21 (1971) 144.
46 C. Giavarini, F. Pochetti and C. Savu, Riv. Combust., 25 (1971) 149.
47 J.M. Powers, R.G. Craig and F.A. Peyton, J. Dent. Res., 48 (1969) 1165.
48 D.J. Harmon, J. Liq. Chromatogr., 1 (1978) 231.
49 F. Noel and L.W. Corbett, J. Inst. Pet., London, 56 (1970) 261.
50 G. Baum and J. Boelter, Fette, Seifen, Anstrichm., 70 (1968) 1.
51 Z. Adonyi, Period. Polytech., Chem. Eng., 10 (1966) 325.
52 Z. Adonyi, in H.G. Wiedemann (Ed.), Proc. 3rd. Int. Conf. Therm. Anal., Davos, 1971, Vol. 1, Birkhäuser Verlag, Basel, 1972, p. 255.
53 Z. Adonyi, Period. Polytech., Chem. Eng., 16 (1972) 285.
54 Z. Adonyi and G. Körösi, in I. Buzás (Ed.), Proc. 4th Int. Conf. Therm. Anal., Budapest, 1974, Vol. 2, Akadémiai Kiadó, Budapest, Heyden, London, 1975, p. 453.
55 Z. Adonyi and G. Körösi, Period. Polytech., Chem. Eng., 19 (1975) 103.
56 J.H. Bae, Soc. Pet. Eng. J., 17 (1977) 211.
57 H.J. Voelker and H. Fischer, in M. Freud (Ed.), Conf. Chem. Chem. Process. Pet. Natur. Gas, Plenary Lecture, Akadémiai Kiadó, Budapest, 1968, p. 650.
58 V. Masek, Wiad. Naft., 5 (1969) 105.
59 V. Masek, Hutn. Listy, 23 (1968) 43.
60 V. Masek, Erdoel Kohle, Erdgas, Petrochem., 21 (1968) 546.
61 V. Masek, Przem. Chem., 47 (1968) 473.
62 V. Masek, Ropa Uhlie, 12 (1970) 496.
63 K. Sobańska and A. Wachal, Tech. Smarow., Trybol., 8 (1977) 41.
64 W.E. House, NLGI Spokesman, 35 (1972) 356.
65 R.D. Novoded, A.P. Lizogub, Yu.L. Ishchuk and M.V. Bogdanov, Neftepererab. Neftekhim. (Kiev), 11 (1973) 32.
66 R.D. Novoded and M.V. Bogdanov, Khim. Tekhnol. Topl. Masel, 19 (1974) 53.
67 R.D. Novoded, M.V. Bogdanov and Yu.L. Ishchuk, Khim. Tekhnol. Topl. Masel, 19 (1974) 59.
68 L.N. Petrova, N.K. Volobuev, E.M. Nikonorov, O.Yu. Galkina and T.V. Semina, Tr. Vses. Nauchno-Issled. Inst. Pererab. Nefti, 24 (1977) 83 (from Ref. Zh., Khim., (1978) Abstr. No. 18, P329).
69 J. Nagy, T. Gábor and E. Brandt-Petrik, in I. Buzás (Ed.), Proc. 4th Int. Conf. Therm. Anal., Budapest, 1974, Vol. 2, Akadémiai Kiadó, Budapest, Heyden, London, 1975, p. 175.
70 R.G. Craig, J.M. Powers and F.A. Peyton, J. Dent. Res., 50 (1971) 450.
71 J. Boelter, Fette, Seifen, Anstrichm., 75 (1973) 593.
72 O.P. Strausz, K.N. Iha and D.S. Montgomery, Fuel, 56 (1977) 114.
73 S.M. Dyszel, Thermochim. Acta, 38 (1980) 299.
74 B.V. Gryaznov, N.G. Orlova and G.V. Shakhsuvarova, Tr. Vses. Nauchno-Issled. Inst. Pererab. Nefti, 10 (1970) 353.
75 J.M. Powers and R.G. Craig, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 3, Plenum Press, New York, 1974, p. 349.
76 J.M. Powers and R.G. Craig, J. Dent. Res., 57 (1978) 37.
77 M.I. Ermolaev, V.V. Batishchev and K.V. Goryachev, Khim. Tekhnol. Topl. Masel, 17 (1972) 46.

78 E. Vámos and T. Flóra, Ropa Uhlie, 9 (1967) 315.
79 D.E. Diskina, I.M. Tiunova, K.M. Badyshtova, E.B. Ivankina, N.I. Grigor'eva and E.E. Obmochaeva, Neftepererab. Neftekhim. (Moscow), 2 (1978) 12.
80 R. Csikós, M. Kántor and L.P. Farkas, Hung. Oil. Gas Res. Inst., 16 (1975) 39.
81 E. Vámos and Z. Adonyi, Ipari Energiagazd., 9 (1968) 80.
82 E. Vámos and T. Flóra, Schmierstoffe, Schmierungstechnik, 27 (1966) 84.
83 E. Vámos and T. Flóra, Ropa Uhlie, 7 (1965) 268.
84 E. Vámos and T. Flóra, Schmiertechnik, 12 (1965) 271.
85 E. Vámos and T. Flóra, Schmierungstechnik, 3 (1972) 210.
86 E. Vámos and T. Flóra, in T. Farkas (Ed.), Corros. Week, Manifestation Eur. Fed. Corros., 41st, Akadémiai Kiadó, Budapest, 1970, p. 721.
87 E. Vámos and T. Flóra, Freiberg. Forschungsh. A, 367 (1965) 267.
88 E. Vámos, F. Mitterhauszer and T. Flóra, Schmiertechnik, 14 (1967) 299.
89 E. Vámos and T. Flóra, Magy. Kem. Lapja, 28 (1973) 393.
90 T. Kapcia and A. Walocha, Nafta (Katowice, Pol.), 33 (1977) 382.
91 I.A. Posadov, N.V. Sirotinkin, Yu.V. Pokonova and V.A. Proskuryakov, Zh. Prikl. Khim. (Leningrad), 48 (1975) 2055.
92 I.A. Posadov, N.V. Sirotinkin, Yu.V. Pokonova and M.V. Vinogradov, Issled. Obl. Khim. Tekhnol. Prod. Pererab. Goryuchikh Iskopaemykh., (1975) 12 (from Ref. Zh., Khim., (1976) Abstr., No. 12, P279).
93 J. Wieckowska and H. Bogdanów, J. Therm. Anal., 17 (1979) 39.
94 E.S. Freeman and W.K. Rudolf, U.S. Nat. Tech. Inform. Serv. AD Rep., 1970, No. 866 489.
95 D.B. Cox and J.F. McGlynn, Anal. Chem., 29 (1957) 960.
96 F.T. Eggerstsen and F.H. Stross, Thermochim. Acta, 1 (1970) 451.
97 P.F. Levy, G. Nieuweboer and L.C. Semanski, Thermochim. Acta, 1 (1970) 429.
98 J.H. Bae, Rev. Sci. Instrum., 43 (1972) 983.
99 N.K. Volobuev, E.M. Nikonorov and A.V. Zubkevich, Tr. Vses. Nauchno-Issled. Inst. Pererab. Nefti, 16 (1976) 67.