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THERMAL ANALYSIS OF LUBRICATING OILS*

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ABSTRACT

Special techniques were used to analyse lube oils; these include low-temperature and pressurized differential scanning calorimetric (DSC) analysis, and modified thermogravimetric analysis (TG) furnace for lube oil density determination.

DSC analysis shows that lube oils contain crystallizable (waxy) and non-crystallizable components (non-waxy). The non-waxy part of the oil displays a glass transition (*i.e.* −90 to −61 °C), which is unaffected by the waxy phase, but is affected by lube oil boiling range. The wax present in lube oils displays a broad dissolution temperature range (*i.e.* −68 to +44 °C), which is dependent on wax composition, and is thus affected by the boiling range and crude oil source. DSC wax crystallization temperatures are shown to correlate with ASTM cloud and pour points. It is also shown that DSC analysis could be used to study oil oxidation.

From the literature it is apparent that thermal analysis can be used to characterize petroleum based materials such as asphalts, lube oils, fuel oils, greases and waxes.

INTRODUCTION

Petroleum products, such as asphalts, fuel oils, lubricating oils, greases, and waxes, are complex mixtures of hydrocarbons. Regardless of the complexity, the petroleum chemist must learn to analyse, characterize and modify these complex mixtures to obtain useful materials. In connection with the characterization of petroleum products, many test procedures have been developed to assist the petroleum chemist. Unfortunately many of these tests are not very reproducible or informative, and are often time consuming. It is the thesis of this paper, that the present state of thermal analysis can provide rapid means of characterizing and testing petroleum products in a more informative manner. We shall discuss the current literature, since it illustrates the rather large area of application in petroleum technology. In discussing our own contributions we will illustrate the potentials by confining the discussion to lubricating oils.

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Literature background

Asphalts. — Voelker and Fischer[1] have used TGA for the microdistillation of crude oil samples in order to indicate the yield of high molecular weight material such as asphalt. Asphalts undergo a glass transition which has been determined by DTA and DSC[2–4]. Petroleum chemists classify asphalts as waxy and non-waxy; however, the quantitative determination of asphalt wax content is both tedious and uncertain[5], and therefore often avoided. We have previously reported the use of DSC to differentiate waxy and non-waxy asphalts[4,6] by detecting the wax melting transition in the asphalt.

Lubricating oils. — Thermal analysis has been used to characterize lubricating oils in terms of transition and degradation. In connection with thermal transitions, lubricating oils contain linear and highly branched hydrocarbons. The linear hydrocarbons readily crystallize to form wax, while the non-linear hydrocarbons do not crystallize or only crystallize very slowly. Thus, during thermal analysis a lubricating oil can display both a glass transition, which is associated with the non-crystallized part of the oil, and phase transitions, which are associated with the wax in the lubricating oil.

Stearns and coworkers[7] have used DTA to determine the glass transition (T_g) of synthetic and natural lubricating oils. The T_g values ranged from roughly -150 to -30 °C, and were used to predict viscosity temperature relationship within the range of 50–100 °C.

Phase transition of wax in oils has been studied by Giavarini *et al.*[8,9] to estimate the paraffin wax content of oils.

The wax crystallization point, which depends on the wax content of the oil, is often determined by an ASTM procedure and is designated as cloud point. The use of thermal analysis to determine the equivalent of cloud point has been proposed[6,10] as a more rapid and reproducible method.

The useful life of the lube oil is determined by its oxidative stability, which is enhanced by hydrogenation of the oil and addition of various oxidation inhibitors. The oxidative stability of the lube oils is assessed by a large variety of tests, which are chosen according to the end use. Many of these tests could probably be replaced, to advantage, by methods which use modern instrumentation. In this connection the use of DSC analysis, using a pressure cell, has been proposed in order to assess oxidative stability of lubricating oils. It has been suggested that the DSC results correlate with an ASTM oxidation test[6,10].

Krawetz and coworkers[11] have used pressurized DTA to determine the thermal cracking temperatures of synthetic lubricants. A similar approach was used by others[12,13] to study the oxidation of various hydrocarbons in the presence of oxidation promoters and inhibitors. Levy *et al.*[14] provided an example for the use of pressured DTA to study the oxidation of motor oils. Lubricating oil additives have their own stability which has been studied especially by TGA[15–17].

Fuel oils. — Oxidation and vaporization of 20 different fuel oils was studied by Vaclav[18] using TGA. The approach identified fuel oils of undesirably high asphaltenes content.

Greases. — Greases consist of nearly 80% oil held in a gel-like state by 20% metal soap, such as lithium stearate. The grease structure, and therefore its useful temperature range, is affected by thermal transitions of the soap. These are events easily determined by DTA or DSC[19–21]. Thermoanalytical techniques could therefore be used to assist in grease processing and quality control.

Waxes. — Hydrocarbon waxes are obtained by the dewaxing of lube oil distillates. The waxes consist of complex mixtures of n-paraffins and iso-paraffins. These materials are easily characterized by DTA or DSC since one is simply measuring melting or crystallization transitions[22,23].

EXPERIMENTAL AND RESULTS

Special techniques

During our work on the thermal analysis of petroleum products a variety of special techniques were used. These include DSC (Perkin–Elmer) techniques for subambient work, high pressure work, and a TGA technique for measuring oil densities.

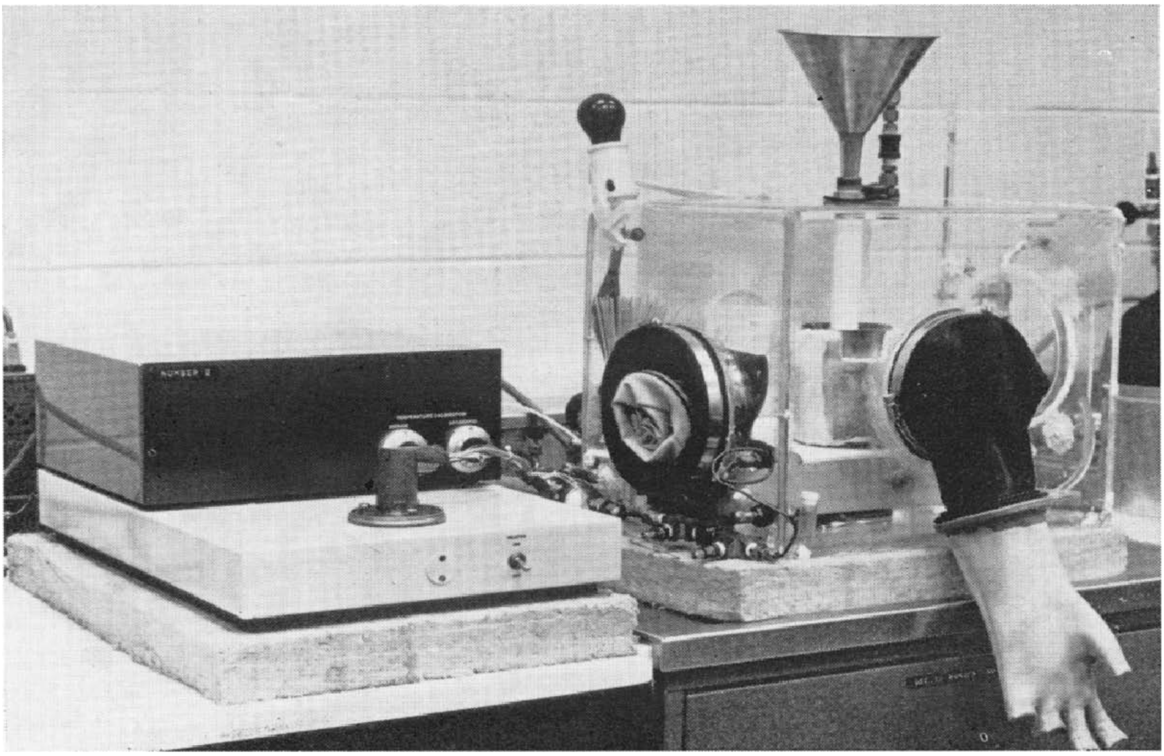

Fig. 1. The Plexiglass dry box DSC accessary.

Subambient DSC. — The thermal analysis of petroleum products must often be done at subambient temperatures and extending to 100°C. Extended use of low temperatures often leads to serious problems associated with accumulation of condensed moisture. In our work, it was necessary to frequently and rapidly analyze oils from −100°C to +100°C. For this purpose, a Plexiglass dry box was constructed, which is shown in Fig. 1.

The system is basically a Perkin–Elmer DSC assembly placed in a dry box and connected to the DSC analyzer by an extension cord, which plugs into the assembly socket on the analyzer. The plug is conveniently made from a discarded DSC assembly. This approach allowed stable baselines and isotherms as low as −97°C. It was also possible to change samples, without first warming to above room temperature. This capability is a considerable time saver.

DSC pressure cell. — The Perkin–Elmer DSC unit is designed mainly for operation at, or near, atmospheric pressure. This unfortunately places a limitation on the areas of application. For example, pressurized DTA systems have been used for determining catalyst activity[24], and motor oil oxidation stability[14]. The advantages of pressurized DSC analysis with the Perkin–Elmer unit was obtained in our laboratory by constructing a simple pressure cell, which is shown in Fig. 2. We have previously reported the use of this cell for lubricating oil oxidation studies[6,10].

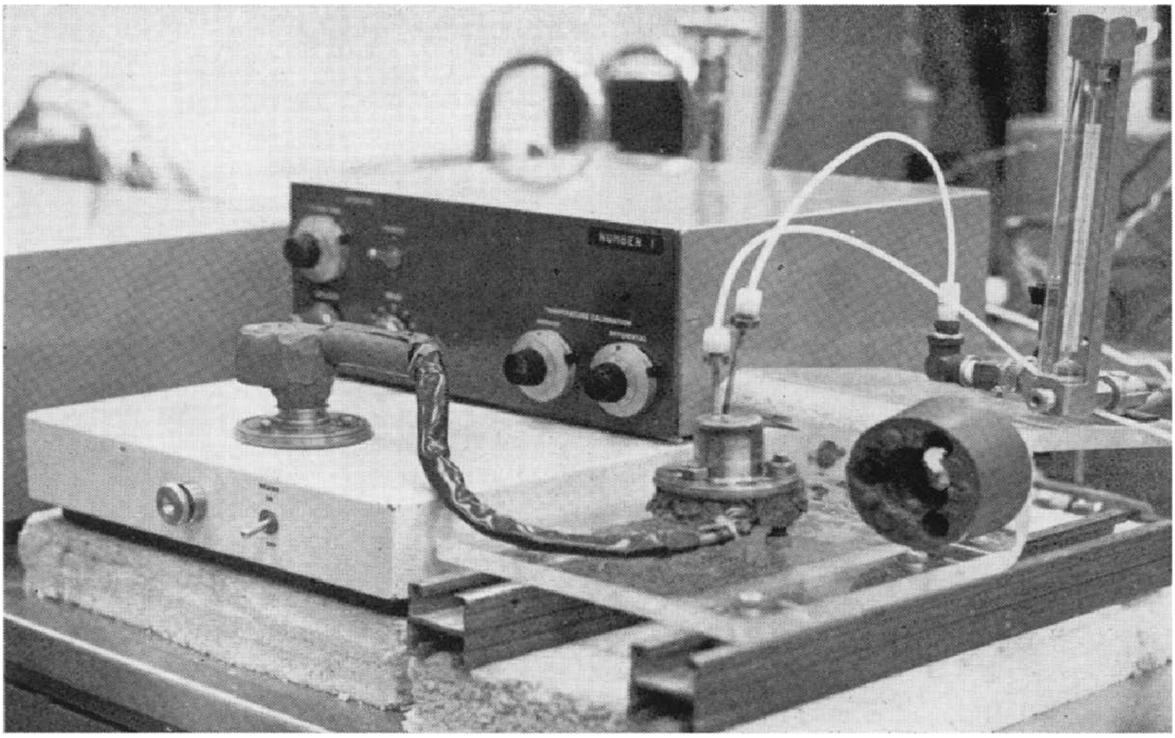

Fig. 2. The DSC pressure cell accessary.

The pressure cell consists of two parts held together by three ½-in. bolts. The bottom part of the pressure cell is the Perkin–Elmer DSC assembly itself. For this application, the purge lines beneath the assembly are plugged. The top of the pressure cell consists of the bottom part of a Perkin–Elmer low temperature cover, with the coolant cup removed. Two lines run through the head for pressurizing and purging the system. The cell has been used, without difficulty, at pressures up to 100 psig.

Density cell. — The Perkin-Elmer thermogravimetric system contains a small furnace nearly the size of a thimble, which in essence is a small cup whose temperature can be controlled. This furnace was used for constructing a cell for quickly measuring the density of lubricating oils at different temperatures. Conventional methods make this an elaborate and time consuming task.

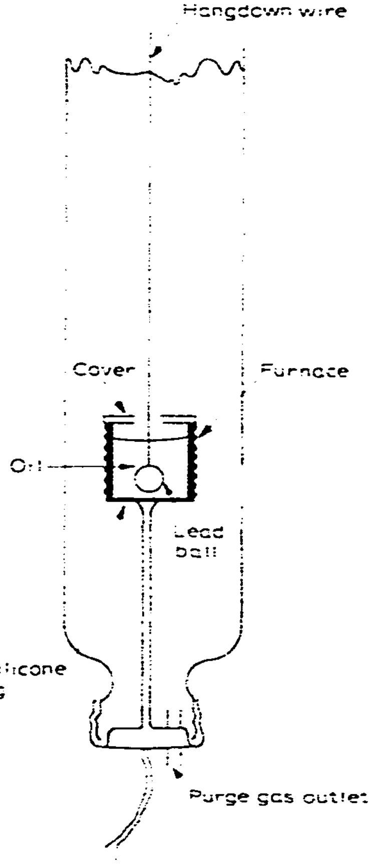

Fig. 3. The Perkin-Elmer TGS-1 furnace adapted for density determinations.

The density cell which was constructed from a Perkin-Elmer TGS-1 furnace is shown in Fig. 3. The furnace as received, is porous and will not hold oil; therefore, it was lined with a thin coating of polysilicone rubber. A volume-calibrated lead plummet was suspended in the oil (approx. 1 ml of oil) and a teflon cover, in the shape of a washer, was placed over the top. This cover minimized surface cooling of the oil sample. The temperature of the furnace was controlled by a UU-1 programmer. A calibration curve was made, which related UU-1 temperature readout and actual oil temperature, as measured by a thermocouple placed in the oil.

Lube oil transitions

Specific heat study. — Lubricating oils often contain normal and iso-paraffins which crystallize to produce what is traditionally referred to as wax. The wax content of the lube distillate can be 20% or less, while the remaining oil consists of highly branched material which crystallizes with difficulty or not at all and therefore forms an amorphous phase. In terms of thermal analysis, therefore, one would expect a phase transition associated with the wax and a glass transition associated with the amorphous phase.

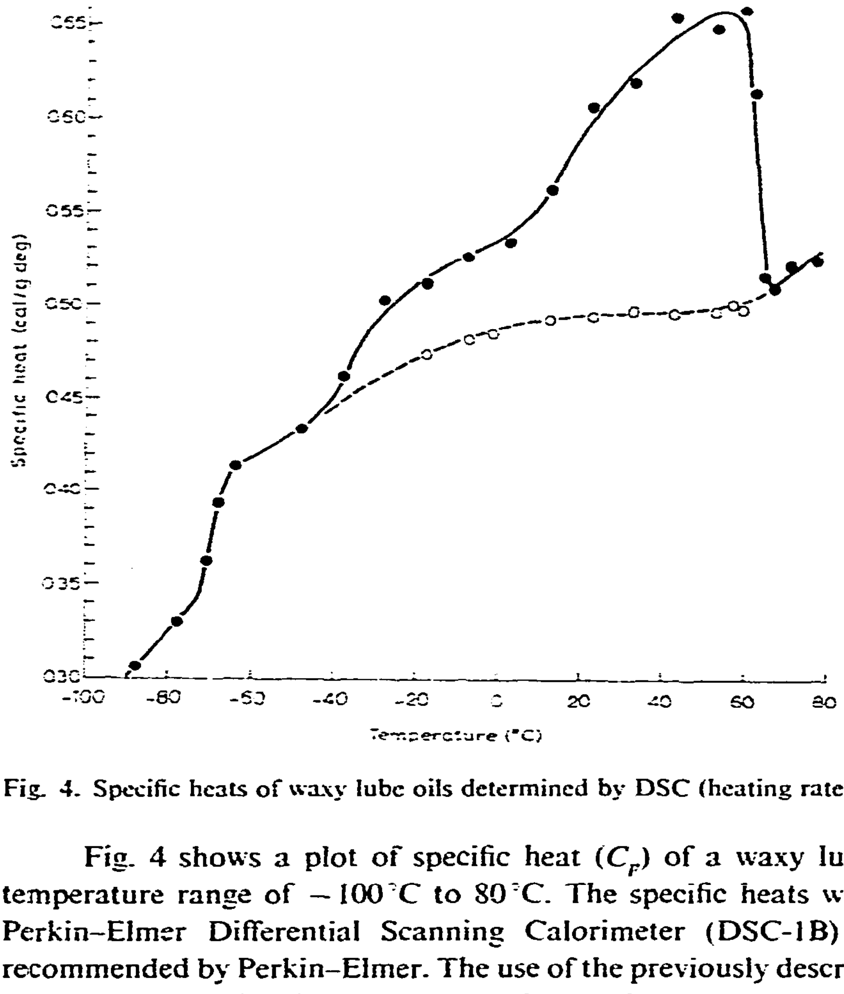

Fig. 4. Specific heats of waxy lube oils determined by DSC (heating rate, 10 °C/min).

Fig. 4 shows a plot of specific heat (C_p) of a waxy lube oil distillate in the temperature range of −100 °C to 80 °C. The specific heats were determined with a Perkin–Elmer Differential Scanning Calorimeter (DSC-1B) using the procedure recommended by Perkin–Elmer. The use of the previously described dry box simplified the analyses, by allowing uninterrupted scans from −100 to +100 °C for the calculation of specific heats.

The curve shows a large change in specific heat (C_p) between −75 and −65 °C, which is interpreted as the glass transition (T_g) of the amorphous portion of the oil. Thus, below −65 °C this particular oil changes to a solid glass, which corresponds to a point where the viscosity approaches 10^{13} poises[25]. Near −50 °C there is another sharp change in C_p, which is interpreted as the onset of wax dissolution. This dissolution process continues up to near 65°C, above which there is a one phase system. These temperature limits define the solubility–temperature relationship.

The dotted line in Fig. 4 represents the estimated specific heat without a heat of transition included. Thus, an endotherm area is defined which is proportional to the heat of fusion of the wax plus heat of solution. Since the process involves hydrocarbons only, the heat of solution is probably small; therefore, this endotherm area is taken as equal to the heat of fusion. The size and temperature range of this endotherm will depend on the type and amount of wax in the oil.

In general practice therefore, DSC heating thermograms of lube oils will have two main characteristics: a glass transition and a wax dissolution transition, unless of course the oil is completely wax free. The subsequent discussions confirm this proposed interpretation.

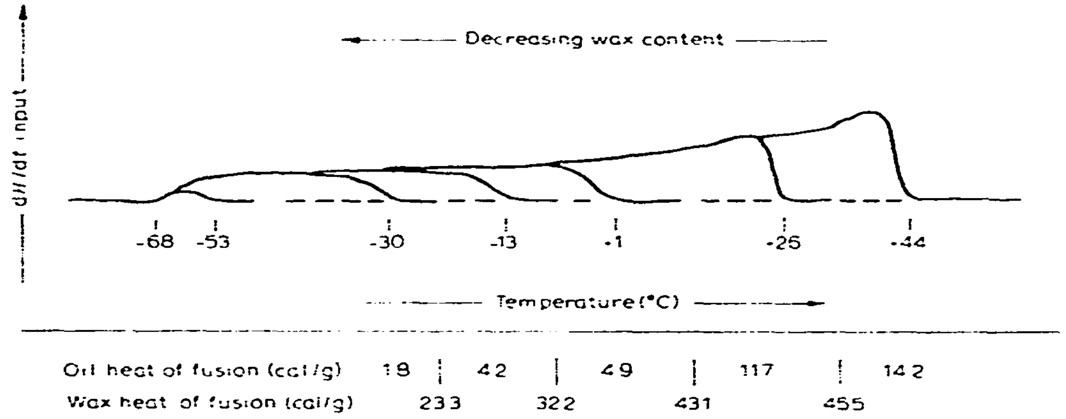

Fig. 5. DSC curves showing the effect of wax content on wax dissolution transition range (heating rate, 10°C/min).

Lube oil dissolution and crystallization transition. — It is well known that petroleum waxes contain a distribution of paraffins, each with its own melting range and heat of fusion. For a waxy lube oil, the temperature range of the wax dissolution process will therefore depend on the paraffin distribution. This point is illustrated by the DSC heating curves shown in Fig. 5. In this study, a lube oil distillate with a boiling range of 360–470°C was successively cooled and filtered at lower temperatures to remove wax fractions. This sequence provided six lube oils each with a different wax content. Four different waxes were also collected.

The DSC curves in Fig. 5 show that for the original lube oil distillate the wax dissolution process was between −68 and +44°C. By removing some wax from the oil the transition range changed to −68–+26°C. The superimposed DSC curves show that decreasing the wax content, by successive cooling and filtering, lowers the upper transition temperature, but not the onset, which remained at −68°C. The decreasing wax content, or change in wax type, is reflected by the decreasing values for heat of fusion from 14.2 cal/g of oil down to 1.8 cal/g of oil.

The waxes which were isolated from the successive cooling steps were scanned on the DSC in order to determine their heats of fusion. The results in Fig. 5 show that with decreasing oil dewaxing temperatures the heat of fusion of the wax obtained decreased from 45.5 to 23.3 cal/g of wax. This is possibly due to changes in wax composition from n-paraffins to isoparaffins with decreasing dewaxing temperatures. Consider C_7H_{16}, where the heat of fusion decreases from 33.5 for n-heptane to 5.4 cal/g for trimethylbutane. The broad endotherm therefore probably depicts the dissolution of first the most soluble most branched alkane to the least soluble most linear alkane.

It is apparent from the heat of fusion values of waxes that they must be used with caution for calculating lube oil wax content. A heat of fusion value applies to the wax obtained under specific dewaxing conditions, and that value cannot be used accurately for other conditions. Each of the oils defined in Fig. 5 was cooled at 10°C/min before obtaining the heating curve. The resultant DSC cooling curves are shown in Fig. 6. The oil with the highest final wax dissolution temperature of +44°C, crystallized at +34°C, while the next oil crystallized at +17°C, etc. Here again, as in the case of the heating curves in Fig. 5, the transition temperature depends on the wax content and type.

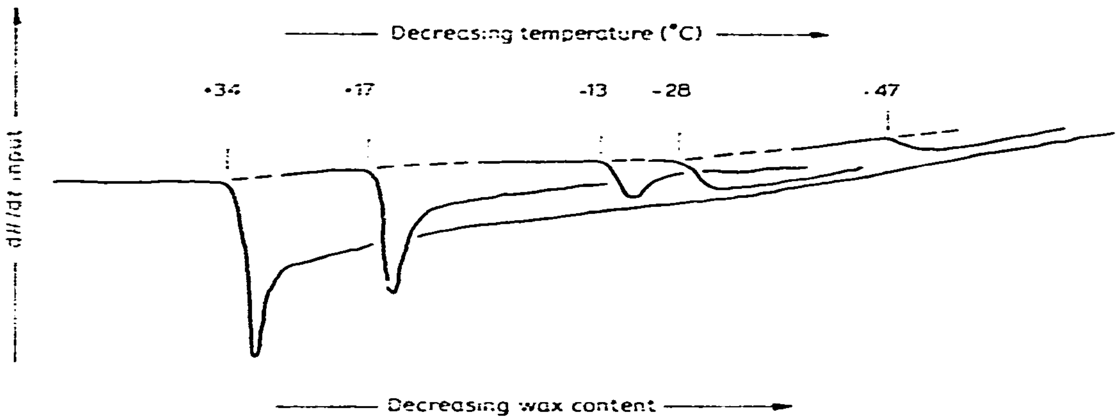

Fig. 6. DSC cooling curves of the oil described in Fig. 5 showing the effect of wax content on crystallization temperature (heating rate, 10°C/min).

Lubricating oils are made as different grades each designed for a specific range of field situations. Definition into grades originates in the initial vacuum distillation of the particular crude oil.

An increase in boiling temperature will yield lube oils with paraffins of higher boiling points. The DSC heating curves for these lube oils are shown in Fig. 7. The figure shows that as the boiling temperature of the oil increases from 300–450°C to 500–600°C the wax dissolution transition temperature range increases from −75–+30°C to −41–+79°C. Changing the lube oil boiling range changes the whole wax transition temperature range; whereas dewaxing a given lube oil will change only the upper temperature of the wax transition.

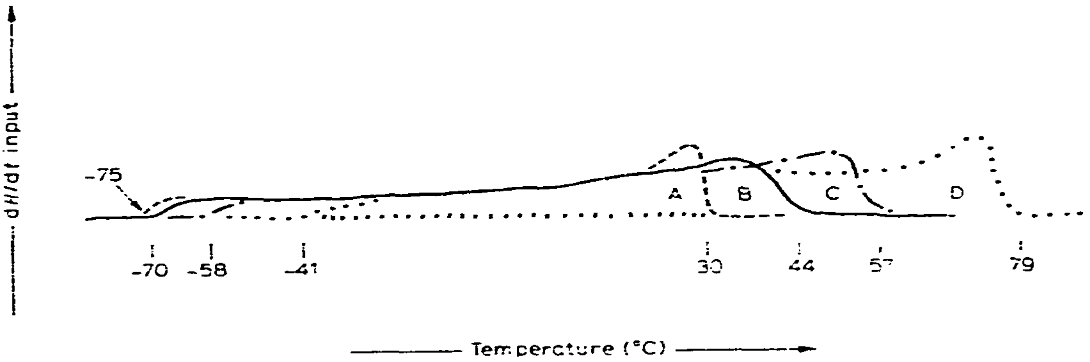

Fig. 7. DSC curves showing the effect of oil grade on dissolution transition temperature range for the oils A–D, having the following approximate boiling ranges: A, 300–450; B, 350–500; C, 450–550; and D, 500–600 °C. (Heating rate, 10 °C/min.)

The lube oils discussed in Figs. 5–7 were all obtained from the same crude oil. Regardless of the boiling range of the original waxy lube oil, the dissolution endotherm has a conspicuous peak like character near the end of the transition. This character presumably depicts a high n-paraffin content for a narrow temperature range. However, different crudes have different compositions, in terms of paraffin type and distribution. Fig. 8 shows DSC heating curves for lube oils obtained from two different

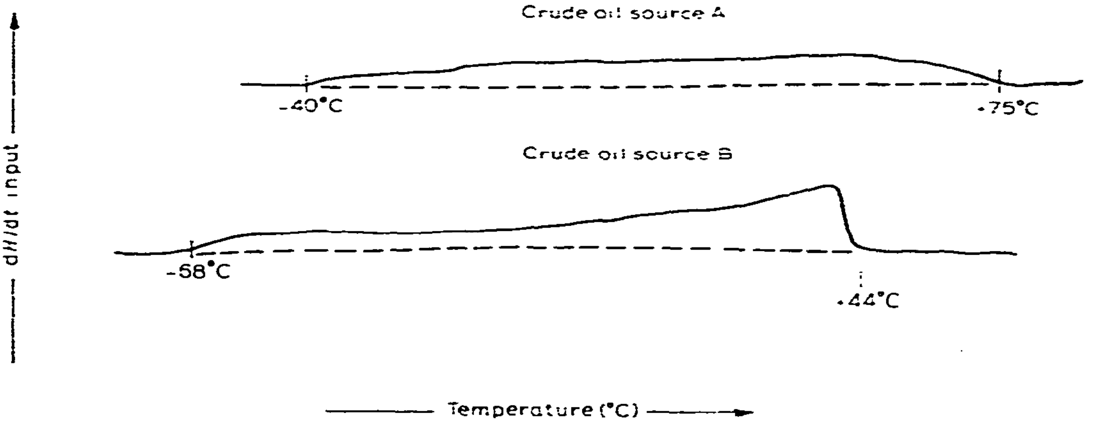

Fig. 8. DSC curves showing the effect of crude oil type on dissolution transition in lube oils (heating rate, 10 °C/min).

crudes. Lube oil A shows a broad rather symmetrical peak, whereas lube oil B has a definitely skewed endotherm. This suggests a conspicuous difference in distribution of paraffin type.

Glass transition. — The preceding discussions were concerned with the thermal behaviour of the crystalline phase in the waxy lube oil. In addition to this phase, the oil contains an amorphous portion. If a lube oil is completely dewaxed, this amorphous portion is the remaining part of the oil. As such, this oil will show increasing viscosity with decreasing temperature, and at some sufficiently low temperature the oil will have a viscosity approaching 10^{13} poises, and will undergo a glass transition[25]. In this transition, there is a drastic change in the degree of freedom for molecular mobility, which is reflected by a sharp change in specific heat; a phenomenon well known in polymer science. From the point of view of the thermal analyst there are therefore two distinguishing features of a lube oil glass transition; (*a*) sharp change in specific heat, (*b*) sharp change in viscosity. Fig. 9 shows two thermograms which display these two features.

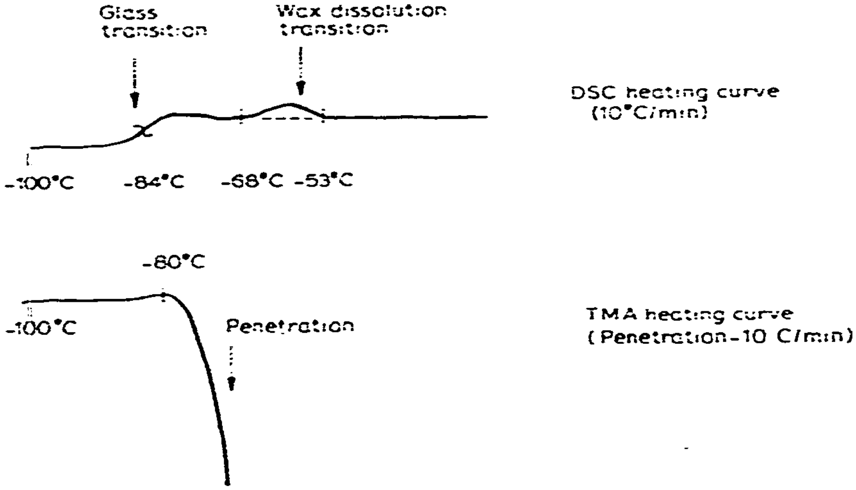

Fig. 9. Determination of the oil glass transition by DSC and TMA.

The top curve is a DSC heating curve of a lube oil containing very little wax (note small endotherm between −68 and −53 °C). Near −84 °C there is a step which corresponds to an abrupt change in specific heat–temperature relationship (see also Fig. 4). The midpoint of this step is taken as the glass transition (T_g) of this oil.

Since the DSC curve shows the oil to have a T_g near −84 °C, it should be hard and impenetrable below this temperature. The second curve shows a penetration curve obtained with a Perkin-Elmer Thermomechanical Analyzer (TMA), using a penetration probe and a 10-g load. The TMA curve shows no penetration on heating from −100 °C to −80 °C at 10 °C/min. However, above −80 °C the glass state is destroyed, the oil softens and the probe penetrates quickly into the sample.

Thus at low temperatures a lube oil can contain two solid phases, (*a*) glass phase, (*b*) crystalline or wax phase. Above the glass transition the oil can contain one fluid phase and a crystalline wax phase. If the oil contains no crystallizable material then there will be only a fluid phase above the T_g. Fig. 10 shows the heating curves for an oil sample which has been dewaxed to decreasing levels of wax, as is indicated by the size of the wax dissolution peak. The curves show that regardless of the wax content the T_g value of the oil remains at −84 °C.

The oil glass transition is however affected by composition and structure of the components in the amorphous phase. This is shown in Table I, where lube oils of

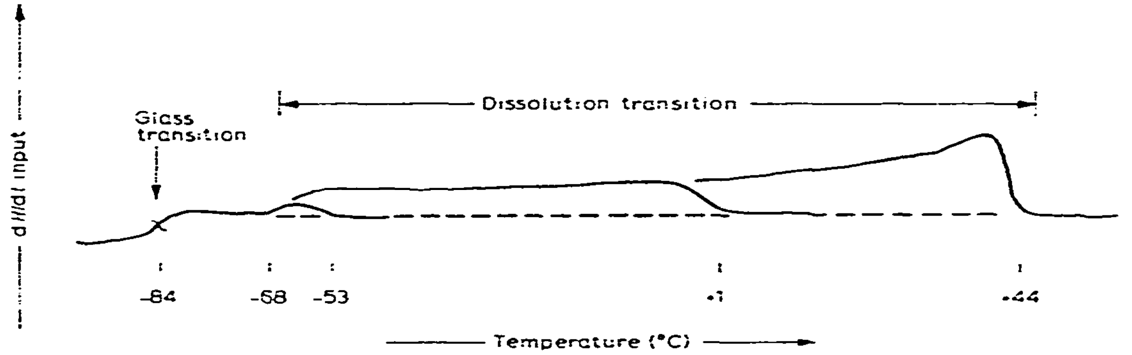

Fig. 10. DSC curves showing the effect of wax content on the glass transition (heating rate, 10 °C/min).

different boiling ranges, but originating from the same crude oil, are compared. The T_g values show an increase in T_g from −90 °C to −61 °C as the oil boiling temperature increases from 300–450 °C to 500–600 °C. Glass transition values for lube oils and various hydrocarbons have been used to predict oil viscosities at different temperatures[7,25].

TABLE I

EFFECT OF BOILING RANGE ON OIL T_g

Boiling range (°C)	*Glass transition (°C)*[a]
300–450	−90
350–500	−84
450–550	−75
500–600	−61

[a] Taken as the inflection point on the DSC T_g curve

The curves in Fig. 10 show a narrow temperature interval between the uppermost temperature of the glass transition range, *i.e.* −80 °C, and the onset of the dissolution transition at −68 °C. Thus on cooling at a relatively fast rate of 10 °C/min there is only roughly 1.2 min for crystallization to be completed in this temperature range. If the crystallization is slow the crystallizable material will remain as an amorphous phase and contribute to the glass transition. On reheating to above the glass transition, as shown in Fig. 11, the crystallizable material will again continue to crystallize. The DSC heating thermogram will therefore show a cold crystallization process just above the glass transition. If, as is shown in Fig. 11, the sample is annealed at the cold crystallization peak temperature, then on rescanning one can obtain a heating curve of the character shown by the dotted line. The endotherm area will of course be increased by an amount equal to the exotherm area.

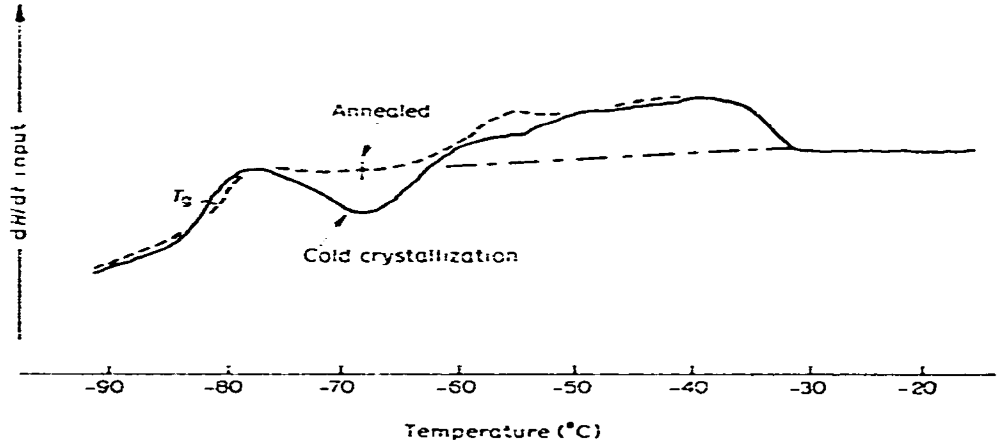

Fig. 11. DSC curves showing the cold crystallization in lube oils (heating rate, 10 °C/min).

Lube oil degradation

We have reported previously[6,10] the use of DSC analysis and a small pressure cell shown in Fig. 2, to determine the thermoxidation stability of lubricating oils. The procedure was shown to be potentially useful for screening antioxidants, and also could correlate with an ASTM method of assessing lube oil stability. It was proposed at a 1970 ASTM D-2 Symposium[6] that the DSC technique could be a more convenient method of testing lube oil stability.

Lube oil density determinations

In the section on Special Techniques we described the modification of a Perkin–Elmer TG furnace to determine the density of lubricating oils at various temperatures. The principle involved was to use the furnace as a cup for the oil. A lead plummet was then suspended from the TG hangdown wire and immersed in the oil (see Fig. 3). The density (D) of the oil at any desired temperature was calculated from the apparent weight change (ΔW) and precalibrated volume of the plummet (V) using the equation $D = \Delta W/V$. The volume of the plummet was determined with the modified furnace, using hexadecane whose density is accurately known at 30, 80 and 100 °C. The temperature of the oil was determined by a calibration of the temperature programmer read out (Perkin–Elmer UU-1) with readings from a thermocouple immersed in the oil.

The sequence used is indicated by the TG thermogram shown in Fig. 12. The plummet is first weighed in air at room temperature, then weighed in oil at room temperature. This provides the apparent weight change at 22 °C. The oil is then heated to the next temperature (*i.e.* 40 °C) at 10 °C/min, then allowed to equilibrate. This provides the next apparent weight change. The total time for the five determinations shown in Fig. 12 was only 40 min.

Table II compares the API and predicted density at 15 °C based on the TG data. The technique is reasonably accurate and rapid; however further refinements are required.

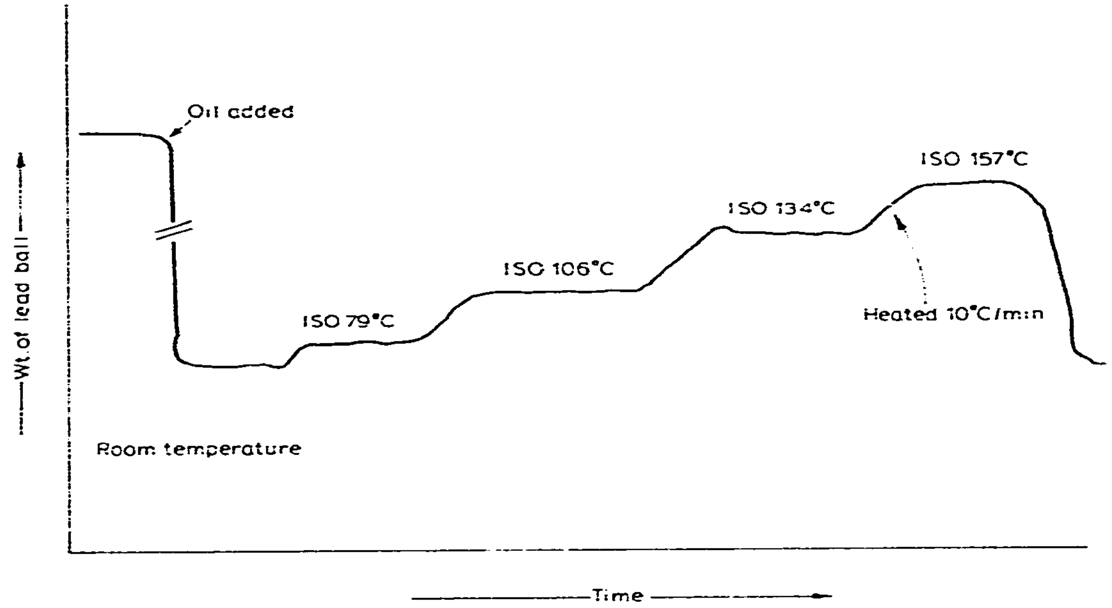

Fig. 12. TG thermogram for the determination of lube oil density at various temperatures. Density, $D = \Delta W/V$.

TABLE II

ACCURACY OF DENSITY MEASUREMENTS

API oil density value at 15 °C	*Extrapolated TG density value at 15 °C*	*Error (%)*
0.8990	0.9246	2.85
0.8618	0.8797	2.07
0.8565	0.8590	0.29
0.845	0.8470	0.24

ASTM cloud and pour correlations

Fig. 6 shows the crystallization exotherms for a lube oil containing different wax contents. The onset of the wax crystallization is a point where there is an abrupt change in the properties of the oil. This definition, which is done on a routine basis by an ASTM or similar procedure, involves a visual observation of the oil as it is cooled slowly to what is referred to as the "cloud point". This thermal event is very easily determined by DTA or DSC and provides the data more quickly and objectively. Another important property is "oil pour point". This is a physical effect where wax crystals of sufficient size and amount (*i.e.* 1%) tend to mesh and effectively cage the oil. This prevents the free flow of the oil thereby leading to clogging of filter screens. Although the DSC or DTA cannot determine this physical effect it might be correlated to wax amount.

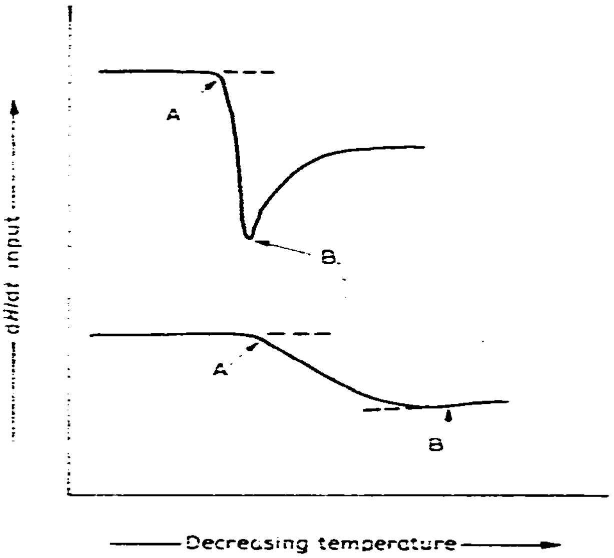

Fig. 13. Definition of the DSC curve points for the ASTM test correlation. A, cloud point; B, pour point. (Cooling rate, 10 C/min.)

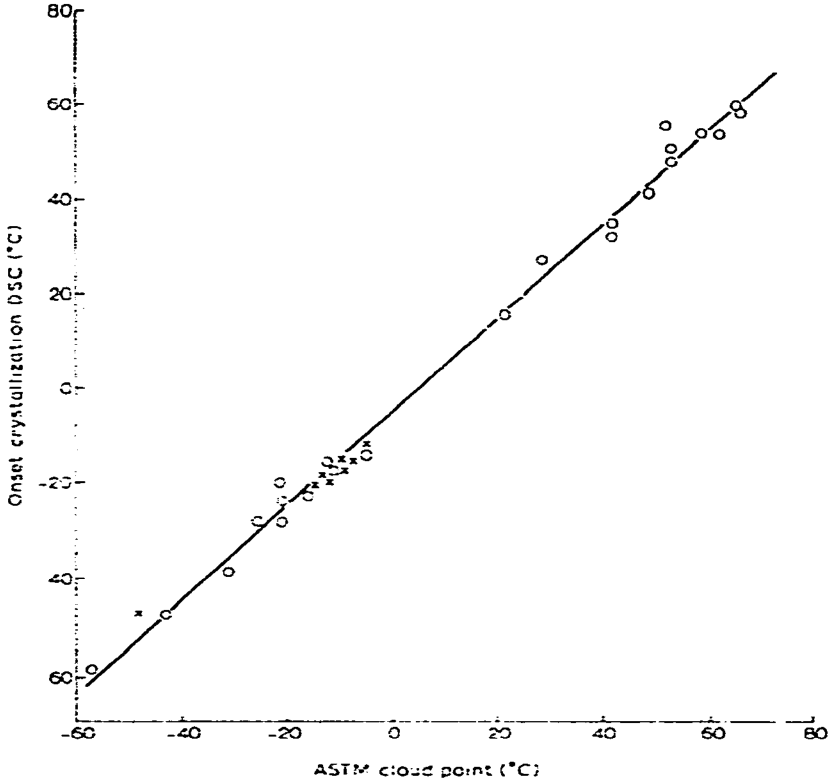

Fig. 14. Correlation of the ASTM cloud point and the DSC crystallization onset, using DSC cooling (10°C/min) and the ASTM cloud point test. (×), fuel oils (2 types); (O), lube oils (11 types).

Fig. 13 illustrates two types of crystallization exotherms obtained by cooling lube oils at 10°C/min. The top curve shows a sharp exotherm starting at A, and forming a peak at B. This peak reflects supercooling, since at slower cooling rates (*i.e.* 2.5°C/min) the peak is nearly absent. The lower curve shows a more gradual crystallization process at the same cooling rate, for an oil which supercools less readily.

In Fig. 14 the onset of crystallization as defined by point A on the DSC curves is compared to the ASTM cloud point for a large variety of oils. The plot shows a good linear correlation between the DSC crystallization onset and ASTM cloud point. The population of samples includes 11 different lube oils and two different fuel oils. The correlation is therefore general for lube oils regardless of the wax type and content. This correlation has been presented at a symposium of the ASTM D-2 committee[6] as a possible future method of defining lube oil cloud points. Rate of data output is very rapid as compared to the ASTM procedure, since some 25–30 determinations per day are possible when using a dry box (see Fig. 1), which removes the need for system warm-up before changing samples.

Point B, as defined in Fig. 13 is taken as the point where sufficient wax has been formed to effect oil caging. The DSC temperatures at B for various oils are compared to ASTM pour points in Fig. 15. The figure suggests a non-linear correlation between

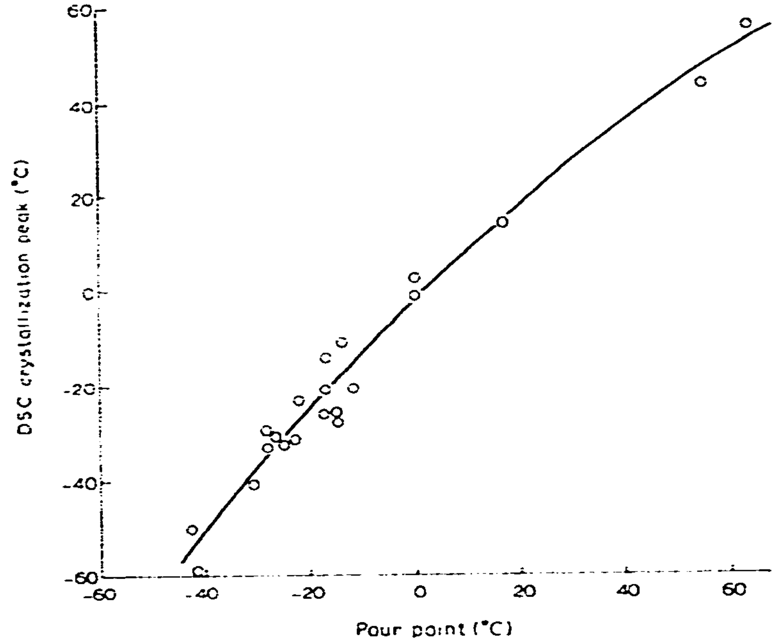

Fig. 15. Correlation of the ASTM pour point and the DSC crystallization peak, using DSC cooling (10°C/min) on six different lube oils.

ASTM pour points for six different lube oils and the DSC data. More data is required at the higher temperature to firm up the correlation. This correlation, if correct, would apply to oils whose pour point has not been affected by the addition of pour depressants. These are agents which decrease the size of the crystals formed, and thereby prevent the physical caging effect; in many cases they do not affect the character of the DSC cooling curve.

CONCLUSIONS

Thermoanalytical techniques such as DSC, DTA, TG, and TMA can be used to determine thermal properties of lubricating oils. The properties demonstrated include specific heats, glass transitions, wax dissolution and crystallization, degradation, and density. These properties are affected by lube oil composition as defined by boiling range and crude source. In addition to lube oil characterization, the technique of DSC is potentially useful for routine testing, *i.e.* cloud points and oxidative stability.

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