

Characterization of oils by differential scanning calorimetry

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Abstract

Lubricating and fuel oils can be characterized for their low-temperature specifications with better repeatability and reproducibility than the standard pour point and cloud point methods. These low-temperature tests are non-destructive and can be followed by using the same sample for measuring the high-temperature thermal stability of the oil (DSC destructive test). The oil sample can be as small as 10 mg. The presence of pour point depressant additives separated the wax crystallization DSC effect (exotherm) from the wax melting effect (endotherm), and also produced heat-flow effect in the higher temperature region. © 1997 Elsevier Science B.V.

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1. Introduction

The pour point method indicates the lowest temperature at which an oil can be stored or handled without congealing in the tanks or pipe lines. This test gave the lowest temperature at which the oil flows under prescribed conditions. However, this test suffers from disadvantages: (a) the pour point depends on the temperature to which the oil was preheated; (b) the repeatability and reproducibility of the test is poor; and (c) the wax skin depends on the oil area and the problem is greatly magnified in case of waxy crudes and oils [1].

The cloud point is the temperature at which the incipient crystallization of wax in the oil results in an opacity or cloud, without complete solidification. At this temperature the oil does not fail to pour.

In this paper, a tentative test examines the cold temperature DSC effects which in contradistinction to the visually measured pour and cloud points accurately determines phase transformations that are highly repeatable and reproducible and also use very small sample weight (cf. 10 mg). In the higher temperature region, thermo-oxidation stability of the oil can be compared [2–4].

2. Experimental

In the low-temperature measurements, accurate data were obtained using a gold sensor (highly sensitive), whereas in measuring the thermal stability, the metal sensor was highly resistive. Samples of 10 mg were placed in uncovered standard Al crucibles in the sample cell of a DSC 30 unit of the Mettler thermo-analytical system TA-3000. The reference cell con-

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tained an empty crucible. Cooling the system to -50°C was achieved using liquid nitrogen. The nitrogen flow rate was adjusted at $60\text{ cm}^3\text{ min}^{-1}$ as purge gas while a programmed heating at a rate of 5 K min^{-1} was used until a final temperature of 125°C . The purge gas was then shifted to oxygen using the same heating rate up to 250°C . Full scale heat flow was 20 mW and a plot of 10 cm was used.

The base oil used (Sample 1) had the properties – density: 0.865 g cm^{-3} , flash point: 189°C , pour point: -3°C , viscosity at 40°C : 20 cS , ASTM colour: 1.5.

Samples 2–5 contained increased quantities of a commercial alkylated polystyrene pour point depressing additive. Samples 6–9 were dewaxed versions of Sample 1. Dewaxing was greater from Sample 6 to 9. The additive increments and wax decrements in successive samples were almost equal.

3. Results and discussion

Fig. 1. shows the DSC thermogram obtained for Sample 1 which is a lubricating base oil. In the low-temperature region, the thermogram exhibits two distinct DSC effects. At the start, the sample was cooled to -50°C . On programmed heating, a relatively low intensity exothermic peak appeared between -8 and -3°C with a maximum at -6°C . This represents the wax crystallization effect, during which the oil exists in the solid phase. Between -4 and 7°C , a second DSC peak with larger intensity, flowing in the endothermic direction, appears with a maximum at around 3°C . On shifting from nitrogen to oxygen purging at 125°C , the

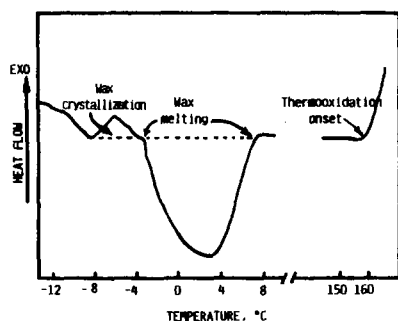


Fig. 1. DSC thermogram of the base oil (Sample 1) showing the wax crystallization exotherm, wax melting endotherm and the thermo-oxidation onset.

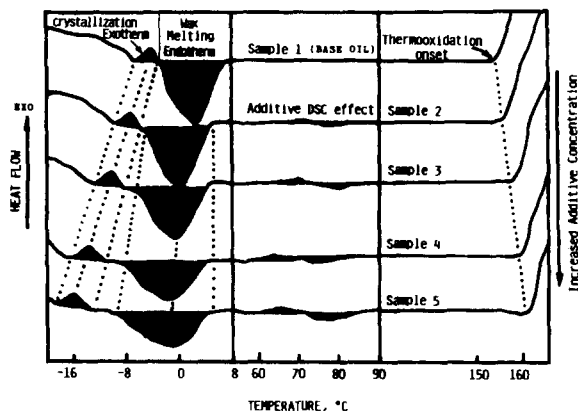


Fig. 2. DSC thermogram of the base oil before and after mixing with progressively increased pour point additive.

thermogram continues with no change in the heat-flow direction up to 157°C , where an exothermic inflection takes place (onset oxidation temperature). The temperature at which the crystallization exotherm is separated from the wax melting endotherm (-3°C) may be considered to represent the pour point of the oil.

3.1. Effect of pour point depressant additive on the oil's DSC behaviour

Fig. 2 compares the thermal response of the base oil (Sample 1) before and after mixing with increased quantities of a pour point depressant additive (Samples 2–5). As the additive is increased in the oil, the wax crystallization exotherm is shifted to lower temperatures, whereas the final temperature of the wax melting endotherm remains approximately unchanged at around 5°C . Hence, the wax melting peak becomes even broader as the additive in the oil increases.

The thermograms of the additive containing samples (Samples 2–5) exhibit some weak DSC effects between ca. 60 and 90°C , which somewhat increase in the intensity as the additive concentration increases. This indicates that these effects are most probably attributed to the additive itself.

The high-temperatures exothermic effect beginning at 157°C for the base oil (Sample 1) is slightly shifted to higher temperatures as the additive concentration increases. This indicates that the additive slightly increases the thermal stability of the oil. This may

Table 1

DSC effect temperature Sample No.	Wax crystallization exotherm			Wax melting endotherm			Thermo-oxidation onset
	Start	Maximum	End	Start	Maximum	End	
1	-8	-6	-3	-3	3	7	157
2	-10	-8	-6	-5	0	5	158
3	-13	-11	-8	-6	-1	5	158
4	-16	-14	-11	-8	-1	5	169
5	-19	-16	-13	-19	-2	5	161
6	-10	-8	-6	-5	0	5	168
7	-13	-11	-8	-6	-1	5	180
8	-16	-14	-11	-8	-1	5	188
9	-19	-16	-13	-10	-1	5	195

be attributed to the aromatic nature of the additive since it is an alkylated styrene polymer. Aromatics are more thermally stable than paraffins. Hence, this additive exhibits dual functionality; i.e., pour point depressing and thermal stabilization.

The better separation of the wax crystallization and wax melting effects with increasing additive concentration appears compatible with Mills observation [1], namely, in the absence of additive, the pour and cloud points are almost coincident, while they diverge as the concentration of the additive increases. Hence, DSC appears useful for detecting pour point additives.

The shift of the crystallization exotherm temperatures, i.e., onset, maximum and end temperatures, seem to have linear relationship with the additive concentration (Table 1). However, Table 2 shows that the magnitude of the endothermic wax melting effect, represented by the ΔH values, does not measurably change with increasing additive concentration.

Table 2
Enthalpy values (ΔH) for the DSC effects, Jg^{-1}

DSC effect	Wax crystallization exotherm	Wax melting endotherm
Sample No.		
1	9.5	212
2	10.1	211
3	10.7	213
4	10.3	213
5	11.0	213
6	9.5	185
7	8.8	152
8	7.2	122
9	6.6	104

3.2. Effect of dewaxing on the oil's DSC behaviour

Another means of lowering the pour point of the lubrication oils is the removal of wax from the oil (dewaxing). This is commonly carried out by adding a solvent such as methylethylketone (MEK) which selectively dissolves the oil at low temperatures at which the wax is separating. Table 1 and Fig. 3 show how progressive dewaxing decreases the lower temperature DSC effects (wax crystallization and wax melting effects), also in a linear manner. Nevertheless, the magnitude of these effects, referred to as ΔH values, is found to decrease, which may be due to the decreasing wax content.

Fig. 3 shows that the thermograms obtained for the dewaxed samples (Samples 6–9) do not contain the

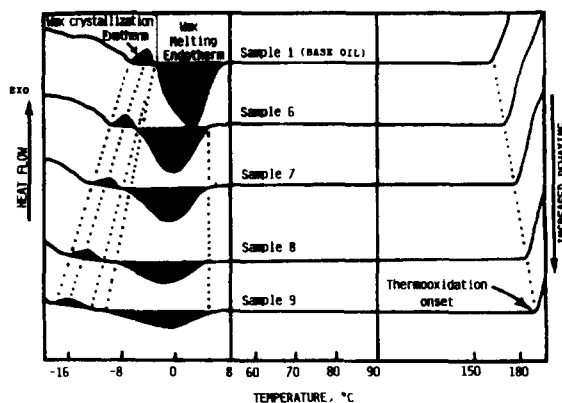


Fig. 3. DSC thermogram of the base oil before and after increased dewaxing with MEK.

weak 60–90°C DSC effects, which proves that they belong to the pour point additive itself.

The DSC thermograms, in Fig. 3, show that the thermal stability of the oil is more significantly enhanced via dewaxing, which is again attributed to the removal of the less stable paraffinic components making up the wax.

4. Conclusions

In this work, a promise has been accomplished towards determining the pour and cloud points with better repeatability and reproducibility than those determined visually, since it is found that these temperatures are close to the start temperature of the wax melting endotherm and the peak maximum of this endotherm, respectively. However, this presumption requires further investigation to precisely limit the

sample weight and the heating rate which are important factors for defining the DSC peak temperatures.

The very high sensitivity and, hence, accuracy of the DSC values, lead to the conclusion that DSC examination of the oils should be very useful as a quality control check, irrespective of dealing with the pour point and cloud point specifications.

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