Thermochimica Acta, 86 (1985) 369–373
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

EVALUATION OF THE THERMAL STABILITIES OF PARAFFIN AND MICROCRYSTALLINE WAX MELTS

DHOAIB AL-SAMMERRAI

Petroleum Research Centre, P.O. Box 10039, Jadiriyah, Baghdad (Iraq)

(Received 26 September 1984)

A knowledge of the thermal stabilities of paraffin and microcrystalline wax melts is of practical importance, especially during their harsh application and when blending them with other petroleum products at elevated temperatures [1].

Evaluation of the thermal stabilities of petroleum and related products is usually performed either statically or dynamically according to standard methods of testing [2], e.g., the bomb method and induction period techniques.

Recently, however [3], thermoanalytical methods such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used extensively in the evaluation of the oxidation stability of petroleum and related products and to study the efficiency of a range of oxidation inhibitors. On heating a sample in air, using a DSC apparatus, an exothermic effect resulting from oxidative degradation is recorded. The onset temperature of the exotherm can be taken as a measure of the thermal stability of the product.

Several workers [4,5] have also used this technique to study the effect of a range of oxidation inhibitors on petroleum products. The higher the onset temperature of the exothermic reaction, the more effective the inhibitor, and conversley.

The purpose of the work presented in this paper is to evaluate the thermal stabilities of paraffin and microcrystalline wax melts using differential scanning calorimetric (DSC) and thermogravimetric (TG) techniques. The work also involved evaluating the efficiency of di-*tert*-butyl-*para*-cresol (DBPC) as an additive for inhibiting the oxidation of these products.

EXPERIMENTAL

Apparatus

The thermal measurements were carried out on a Heraeus TA 500 thermal analyser. In the DSC determinations, wax samples weighing 5–10 mg were

0040-6031/85/$03.30

TABLE 1

Specifications of the waxes

Specification	Paraffin	Microcrystalline
Grade	A	A
Penetration (25°C)	12	12
Oil content (wt%) max.	0.9	2.0
Melting point (°C)	64–68	71–75
Colour ASTM D-1500 max.	–	4.0

heated at a rate of 10°C min^{-1} in an aluminium sample crucible under static air atmosphere. The reference cell was left empty. TG and DTG curves were recorded simultaneously by placing a sample weighing 10–15 mg in a platinum crucible and heating at a rate of 20°C min^{-1} under nitrogen gas flowing at a rate of 10–15 $\text{cm}^3\ \text{min}^{-1}$. All measurements were carried out in triplicate.

Materials

Grade A paraffin and microcrystalline waxes were supplied by a local refinery. Specifications of these waxes are given in Table 1. Standard benzoic acid and tin were used in calibrating the DSC apparatus. DBPC (Topanol) of more than 98% purity was purchased from the ICI Chemicals Company.

Procedure

Different concentrations of DBPC in paraffin and microcrystalline waxes were prepared by thorough mixing of the additive with a hot melt of the wax (80°C) until it was completely dissolved.

RESULTS AND DISCUSSION

The DSC curves of the paraffin and microcrystalline wax melts are shown in Fig. 1. The onset temperature of the exothermic effect is usually evaluated by extrapolating the tangents of the DSC curve as shown in the same Figure.

It is obvious that the microcrystalline wax possessed a higher onset temperature of oxidation (214°C) when compared to that of the paraffin wax (193°C), i.e., the former wax is of a higher oxidation stability. This behaviour could be attributed to the fact that the microcrystalline wax is richer in its aromatic content (~ 0.8 wt%), while the paraffin wax content of aromatic compounds does not exceed 0.2 wt%. The aromatic compounds are well known to act as natural oxidation inhibitors [6].

It is also clear from Fig. 2 that on addition of Topanol in concentrations ranging from 50 to 150 ppm to the paraffin wax, an improvement in the onset temperature of oxidation of 17°C was achieved. The onset temperature of the paraffin wax containing 150 ppm Topanol was almost similar to that of untreated microcrystalline wax.

However, only a slight improvement in the onset temperature was noticed upon the addition of Topanol to the microcrystalline wax even at the 150 ppm level (5°C), as shown in Fig. 3. This indicated only a weak effect of this additive as antioxidant in microcrystalline wax.

Figure 4 is a plot of the onset temperatures of oxidation against different concentrations of Topanol in the waxes.

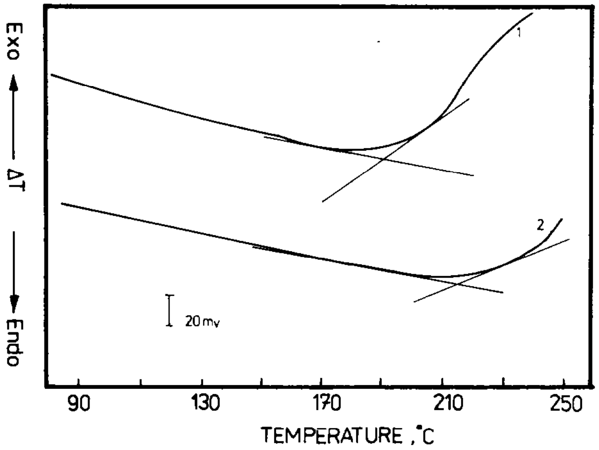

Fig. 1. DSC curves of the oxidation of (1) paraffin wax and (2) microcrystalline wax.

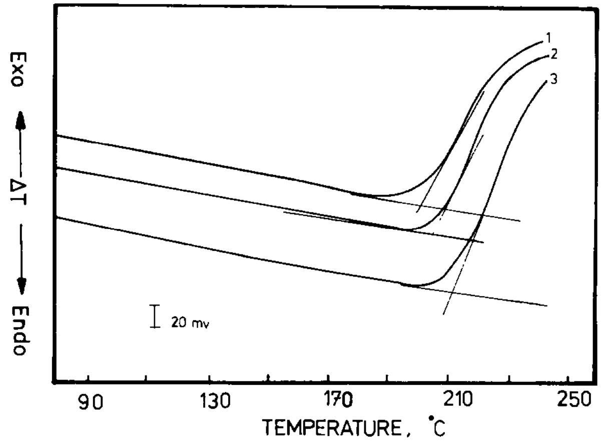

Fig. 2. DSC curves of the oxidation of paraffin wax in the presence of (1) 50 ppm Topanol, (2) 100 ppm Topanol and (3) 150 ppm Topanol.

The results achieved when using the DSC technique in studying the oxidation stability of paraffin and microcrystalline wax melts correlated well with those obtained from another method of evaluation performed by a local refinery [7].

Thermogravimetry (TG) and differential thermogravimetry (DTG) were also recorded simultaneously for the two types of waxes and typical traces are displayed in Fig. 5. Transition temperatures for the paraffin waxes were: $T_{\text{initial}} = 225°\text{C}$, $T_{\text{max}} = 387°\text{C}$ and $T_{\text{final}} = 475°\text{C}$, while for the microcrystal-

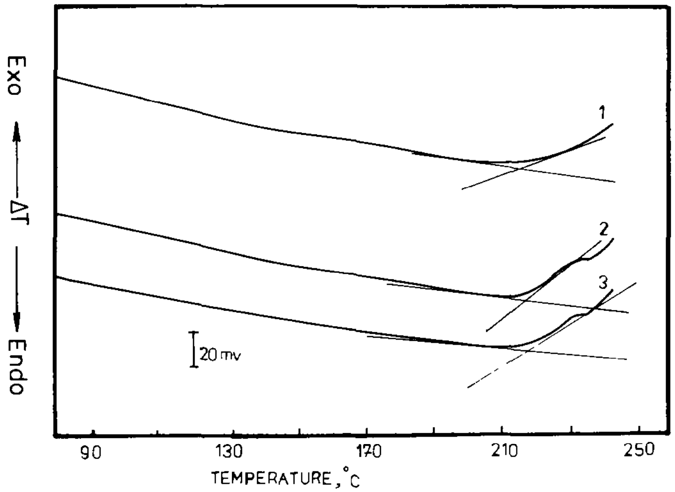

Fig. 3. DSC curves of the oxidation of microcrystalline wax in the presence of (1) 50 ppm Topanol, (2) 100 ppm Topanol and (3) 150 ppm Topanol.

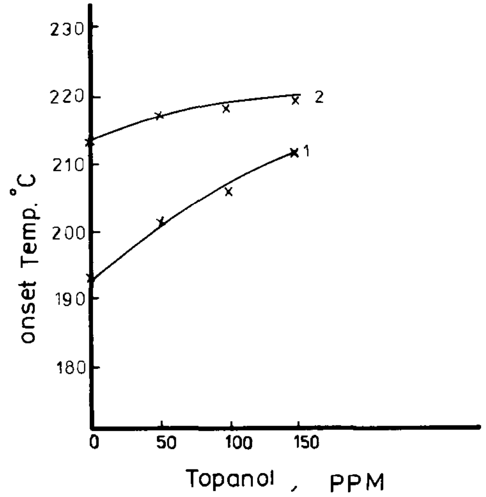

Fig. 4. The improvement in the oxidation stability upon addition of Topanol to (1) paraffin wax and (2) microcrystalline wax.

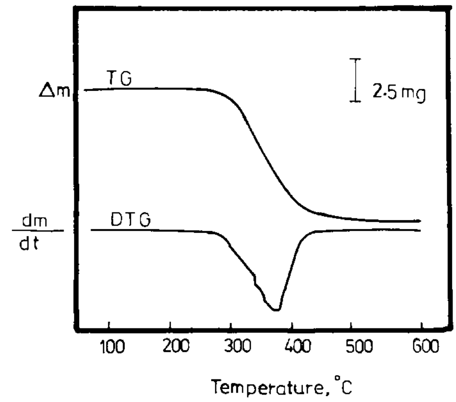

Fig. 5. Typical TG and DTG curves of the waxes.

line wax they were as follows: $T_{\text{initial}} = 300°\text{C}$, $T_{\text{max}} = 435°\text{C}$ and $T_{\text{final}} = 500°\text{C}$. These results were recorded from the DTG trace.

The weight loss of these waxes under the inert atmosphere of nitrogen gas corresponds mainly to volatilization. It is obvious from the results obtained that the microcrystalline wax is of a higher thermal stability when compared to that of the paraffin wax. This behaviour is related to the average molecular weight of these products, i.e., the microcrystalline wax has a higher average molecular weight (490) than that of the paraffin wax (435).

It can be concluded that the DSC technique, which was used successfully for the first time in the evaluation of the oxidation stability of this type of petroleum products, and thermogravimetry proved to be quick, reproducible and simple methods when compared to other means of evaluation, and they require only very small amounts of sample.

REFERENCES

1 G.D. Hobson, Modern Petroleum Technology, Applied Science Publishers, London, 1975.
2 Institute of Petroleum Standards for Petroleum and its Products, Applied Science Publishers, London, 1982.
3 F. Noel, Thermochim. Acta, 4 (1972) 377.
4 C. Giavarini and F. Pochetti, J. Therm. Anal., 5 (1973) 83.
5 M.M. Barbooti and D. Al-Sammerrai, Thermochim. Acta, 76 (1984) 221.
6 I. Wahaiab, D. Al-Sammerrai, K. Al-Janabi and M. Ibrahim, Production of Transformer Oil According to BS 148/1972, Paper Presented at the Scientific Conference on Petroleum Research and Industries, Baghdad, 1980.
7 Private communications, 1983.