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INVESTIGATION OF THE THERMO-OXIDATION STABILITY OF LUBRICATING BASE OILS AND COMMERCIAL ENGINE OILS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The thermo-oxidation stabilities of four Arabian lubricating base oils and several commercial engine oils of various grades have been examined by differential scanning calorimetry. Oxidation onset temperatures were determined and used as the criterion for the beginning of oxidation in the oils. Correlation of the onset temperatures for the base oils with various characteristics of lubricating oils may indicate that increased amounts of resinous materials are present, increasing oxidation stability and increasing the boiling range of the oils. Several commercial engine oils of various grades have also been examined.

INTRODUCTION

Lubricating oils are attacked by oxygen in air during use at relatively high temperatures. This thermo-oxidation can be delayed by the addition of stabilizers (antioxidants). The temperature at which an oil starts oxidation depends on the chemical composition of the oil, and measurement of the oxidation stability of lubricating oils is therefore an important parameter for quality control at increased temperatures.

Under dynamic conditions, the onset temperature of oxidation in a differential scanning calorimetry (DSC) unit can be used to characterize oxidative degradation of oils [1]. However, other workers have used thermogravimetry (TG) to compare the processes of thermal oxidation of base oils, by observing the temperatures at which 5, 10 and 50% mass decrements occur [2]. Methods involving TG mass loss and differential thermal analysis (DTA) of the area of the exothermal effect have also been used [3].

In the present work, oxidation onset temperatures for several base oils and engine lubricating oils have been determined by DSC, in order to correlate their oxidation stabilities.

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EXPERIMENTAL

The oils

Base oils

Three base oils with increasing boiling ranges, designated 100 SN, 300 SN and 700 SN, produced by the Saudi Petromine Oil Company via vacuum distillation of crude oil(s), and a bright stock, designated BSS, produced by deasphalting a short residue with propane, were used in this study. These oils were dearomatized using furfural and dewaxed using methyl ethyl ketone. The technical properties density, color, flash point, pour point and viscosity were determined for the four base oils using ASTM standard methods ASTM-D 1298, ASTM-D 1500, ASTM-92, ASTM-97 and ASTM-D 445, respectively. Densities were determined at 15.0 °C. The viscosities of the base oils 100 SN, 300 SN and 700 SN were determined at 40.0 °C, but the viscosity of BSS was measured at 100 °C (32.0 cS). Flash and pour points were taken in °C.

Commercial engine oils

Eight commercial engine lubricating oils were studied; two single-grade (SAE 40) oils, produced by Mobil and Balbied; two multigrade (SAE 30W40) oils, produced by Shell and Nissan; and four extrasuper multigrade (SAE 20W50) oils, produced by Mobil, Shell, Petromine and Nissan.

DSC thermo-oxidation testing

9.0 mg of each of the oils was placed in an uncovered standard aluminium crucible in the sample cell of a DSC-30 unit (TA 3000 Mettler system). The

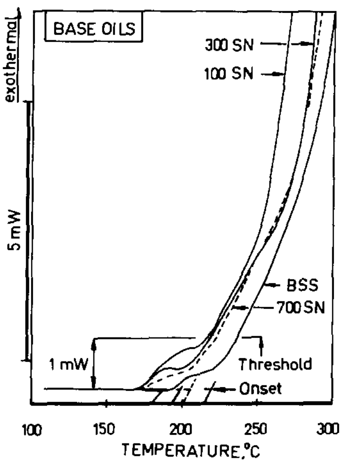

Fig. 1. DSC oxidation thermograms showing onset temperatures for lubricating base oils.

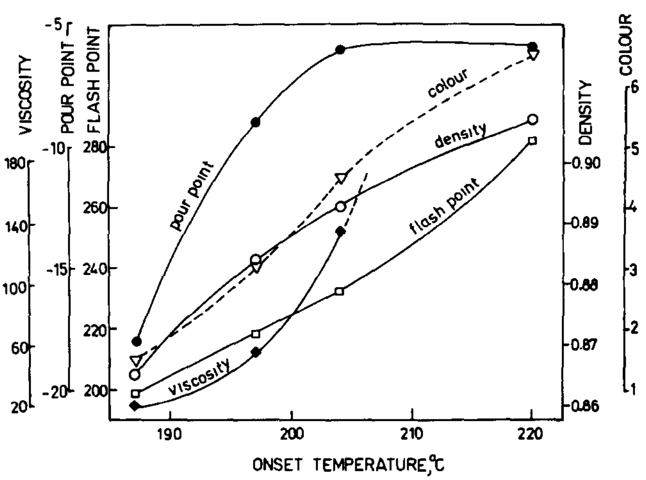

Fig. 2. Relations between technical characteristics of lubricating base oils and their oxidation onset temperatures.

reference cell contained an empty uncovered crucible. Oxygen with a flow rate of 60 cc min^{-1} was used as the purge gas. The DSC unit was operated at initial temperature, 100° C; heating rate, 10 K; final temperature, 300° C; and full scale range, 10 mW.

A regression line was drawn to follow the DSC curve before the start of oxidation (baseline). A tangent to the deflected exotherm was drawn at a threshold value (1 mW of the baseline), and the intersection point of the two lines was taken as defining the oxidation onset temperature (see Fig. 1).

RESULTS AND DISCUSSION

A threshold value is used in DSC measurements of the oxidation onset temperature in order to exclude variations in DSC response resulting from changes in sample weight [1]. However, a fixed weight of 9.0 mg was used for all measurements in the present work. The onset temperatures obtained for the base oils designated 100 SN, 300 SN, 700 SN and BSS are illustrated in Fig. 1. These onset temperatures increase with increasing boiling range of the base oils. Figure 2 shows a plot of a number of significant lubricating oil characteristics vs. oxidation onset temperature as measured by the DSC method. The values of all these characteristics, which normally increase as a function of increasing boiling range of the base oils, were found to increase with increasing oxidation onset temperature. Although the base oils under investigation were dearomatized and dewaxed, they still contained resinous materials that increase in the base oils with increasing boiling range. Paczuski and Kardasz [2] found that resins in base oils act as natural oxidation inhibitors. Hence, the trend of significantly increasing viscosity and slowing down of pour point (Fig. 2) with increasing oxidation onset

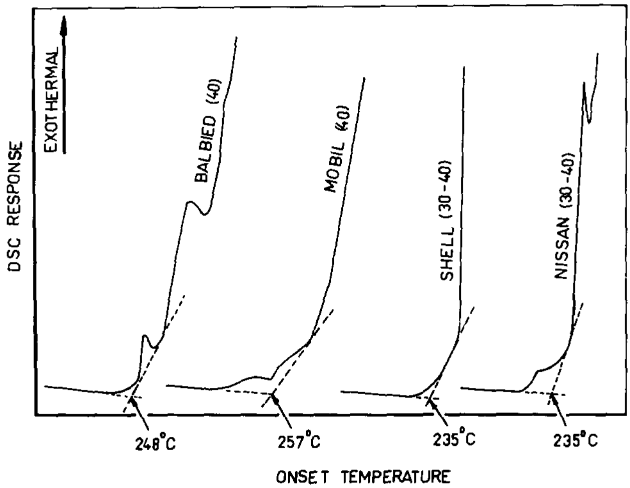

Fig. 3. DSC oxidation thermograms for single-grade (SAE 40) and multigrade (SAE 30W40) engine oils.

temperature is indicative of the presence of increasing amounts of resinous materials.

Figure 3 shows the thermal oxidation stabilities of two single-grade engine oils (SAE 40) and two multigrade oils (SAE 30W40). The single-grade oils have higher oxidation onset temperatures than the multigrade oils. Furthermore, the extrasuper multigrade engine oils (SAE 20W50) appear to have lower onset temperatures than the multigrade (SAE 30W40) and single-grade oils (see Figs. 3 and 4). This is more obvious on comparing oils of different grades produced by the same oil producer. Thus, the Mobil extrasuper multigrade oil has an onset temperature of 222°C (Fig. 4), whereas the

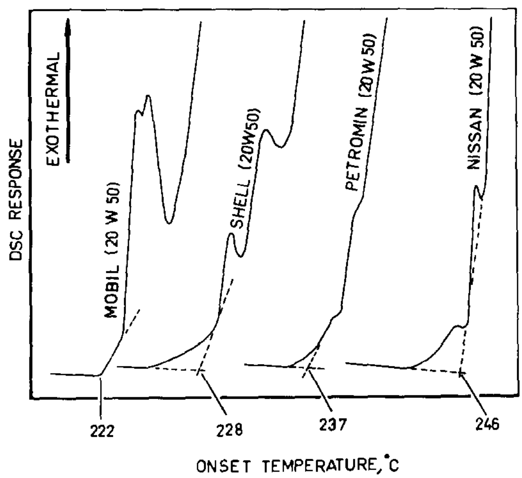

Fig. 4. DSC oxidation thermograms for extrasuper multigrade (SAE 20W50) oils.

single-grade Mobil oil gives 257 °C (Fig. 3). Similarly, the Shell extrasuper multigrade oil has an onset temperature of 228 °C (Fig. 4), whereas the Shell multigrade oil gives 235 °C (Fig. 3). This may indicate that the Mobil and Shell companies use the same base oils or blend of base oils in preparing their oils of different grades, but then add to each different packages of additives of various purposes, e.g. antioxidants, anti-wear anti-rust and anti-foam additives, pour-point depressants, viscosity-index improvers, detergent-dispersant additives, etc. In the extrasuper multigrade oils, the package of additives contains more components in larger amounts. Some of these additives give antagonistic responses to antioxidants, i.e. decrease oxidation stability. For instance, the widely used antioxidation zinc dialkyldithiophosphate gives relatively lower oxidation stability on the addition of the detergent-dispersant additives poly(isoalkenyl succinimide) and/or overbased sulfurized calcium phenate [4]. Most oil producers consider oil superiority to be based on increased viscosity index—hence, the names "multigrade" and "superextra multigrade", which are based on grades of viscosity index rather than on any other characteristic.

On the other hand, the Nissan extrasuper multigrade engine oil 20W50 gives a higher oxidation onset temperature (246 °C) than its multigrade equivalent 30W40 (235 °C). This may be due to the use of different base oils to ensure synergism between the additive package and the base oil hydrocarbons [5]. Nissan may also have considered oxidation stability to be the leading characteristic in compounding extrasuper engine oils. Petromine engine oil seems to possess a high thermal stability compared to Mobil and Shell engine oils.

It is evident from Fig. 4 that the lower the oxidation onset temperature (i.e. the lower the stability) of an engine oil, the more distinct the isolation of a peak or peaks just beyond the onset inflection in the DSC thermogram. Such a peak, or shoulder in the case of more stable oils (cf. Petromine and Nissan oils, Fig. 4), indicates the amount of easily oxidizable oil components.

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