

Oxidation Stability and Antioxidant Capacity of Lubricants Measured by a Pressure DSC

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A methodology was developed for evaluation of oxidation stability of base stocks and engine oils. Analytical procedures for both classes of lubricants were based on the ASTM standards D 6186 and/or E 2009. The procedures were applied to a set of engine oils of the SAE 5W-30 specification, and to a set of several hydrocracked and solvent neutral base oils, both with and without addition of antioxidant. A potential of a pressure DSC for diagnostic purposes was also demonstrated by monitoring the engine oil ageing during its operation in heavy-duty engine.

Keywords : base oil, engine oil, oxidation stability, pressure DSC

1. INTRODUCTION

Differential scanning calorimetry (DSC) was used for evaluation of oxidation stability of lubricating oils as early as in the sixties. However, the large potential of DSC could be exploited only in the nineties after the pressure DSC (PDSC) became available. Analysis under increased pressure brought a better baseline stability due to a limited evaporation of samples and the analysis time was also shortened. One of the first applications of the pressure DSC technique was published in 1980 [1].

PDSC allows a variable temperature programs and a choice of oxidizing gas (oxygen, air) for analyses and, therefore, evaluation of oxidation stability of lubricating oils can be done under isothermal as well as non-isothermal conditions. Effects affecting the oil oxidation in the PDSC cell were evaluated and described [2-3]. Analytical procedures for evaluation of oxidation stability of lubricating were also standardized and the two most popular standards are the ASTM D 6186 and E 2009 corresponding to the isothermal and non-isothermal techniques, respectively. The PDSC test CEC-L-85-T-99 is also one of the tests included in the specifications ACEA E5 and Global DHD-1 for engine oils for heavy-duty engines.

2. EXPERIMENTAL

2.1 Isothermal analysis ASTM D 6186

About 3 mg of a sample is weighed into a standard open Al crucible and placed in the measuring cell. Temperature of the cell is increased from the ambient temperature to 210 °C at a rate of 100 °C/min and allowed to equilibrate for 2 min. After that period the cell is pressurized by oxygen to 3.5 MPa and the purge gas flow rate is adjusted at 100 mL/min. The oxidation induction time (OIT) is measured from the time the oxygen valve was opened. Detection of OIT is made by an extrapolation of the DSC signal when a strong exothermic reaction (oxidation) is detected (see Fig. 1). When short OIT below 10 min is detected, the oxidation temperature should be decreased to 180 °C (further to 155 °C and 130 °C).

2.2 Non-isothermal analysis ASTM E 2009

Again about 3 mg of a sample is prepared as in the previous method. Temperature is increased from ambient by a gradient

of 10 °C/min. Oxygen pressure is maintained at 3.5 MPa from the start of heating. Flow rate is adjusted to 50 mL/min. A similar signal to that in Fig. 1 is obtained and the oxidation onset temperature (OOT) is evaluated.

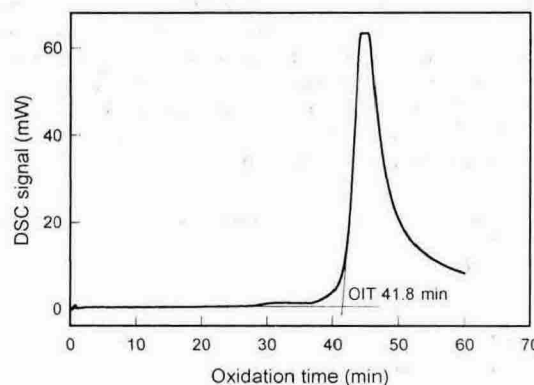


Fig. 1 Pressure DSC analysis of engine oil

3. RESULTS AND DISCUSSION

3.1 Engine oils

Engine oils were analyzed by the isothermal procedure according to ASTM D 6186. However, the temperature of PDSC analysis was decreased by 10 °C, which led to approximately doubled OITs. According our experience, temperature of 200 °C is more suitable for modern engine oils. Analyzing more than 60 engine oils of different specifications and from different producers the OITs obtained were all in the range from 17 min to 80 min. This range allows very well differentiating between individual oils.

Oxidation induction times express the potential of engine oil to fight against oxidation. During the induction period, oxidation reactions and oxidation extent are influenced by antioxidants. Even after consumption of the antioxidants the hydrocarbon chains can be oxidized by a radical mechanism and an exothermic effect can clearly be seen in the DSC output signal (Fig. 1). The OIT can thus be considered as a factor that is somewhat proportional to the antioxidant capacity of engine oils and other lubricants.

PDSC analysis is powerful, for example, in comparing oxidation stability of engine oils. In Fig. 2, there is a comparison of oxidation stability of SAE 5W-30 oils from different producers expressed as OITs from PDSC analysis.

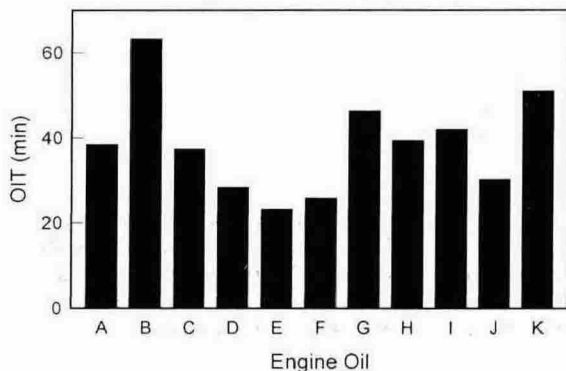


Fig. 2 Oxidation stability of SAE 5W-30 engine oils by PDSC

There were large differences between OITs of individual engine oils. Whereas oils with the European specification ACEA A3/B3,B4 had very good oxidation stability, among oils with the specification ACEA A1/B1 and with HTHS viscosity < 3.5 mPa.s there were some oils with rather poor oxidation stability (see oils E and F in Fig. 2).

Another example of PDSC utilization can be in the field of diagnostics [4,5]. In Fig. 3 there is shown a decrease of OIT during operation of oil in a heavy-duty engine. Normal drain interval of that oil is 40 000 km, however, the oil was operated for up to 67 000 km. There is clearly an exponential decay of OITs showing that much of the antioxidant capacity of engine oil was consumed during the first 20 000 km.

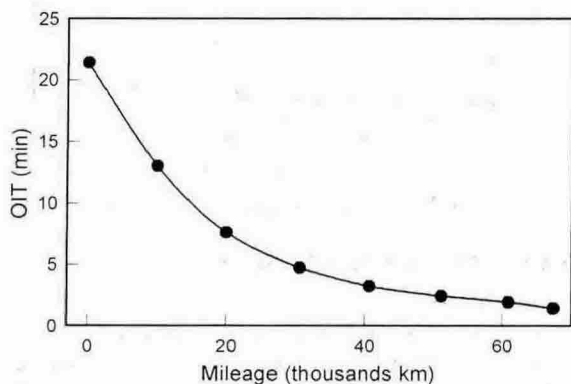


Fig. 3 Decrease of OIT during operation of engine

3.2 Base oils

Usage of an isothermic procedure is not the best choice for evaluation of oxidation stability of base oils. The OITs are very low, below 5 min, even if temperature is lowered to about 170 °C. Moreover, lower temperatures lead to a broad DSC signals with a low intensity. The better choice is the non-isothermal procedure that leads to a similar signal as in Fig. 1. A disadvantage of the non-isothermal method is a possibility of larger experimental errors. Most of base oils have their OOTs between 190 °C and 230 °C. It means that OOT of those base oils are detected within 4 minutes at the gradient of 10 °C/min. There is much less opportunity to distinguish between two base oils with close oxidation stability.

In Fig. 4, there is shown a comparison of oxidation stability for several base oils, hydrocracked as well as solvent neutral, and for the same oils with 0.4 wt % of antioxidant BHT.

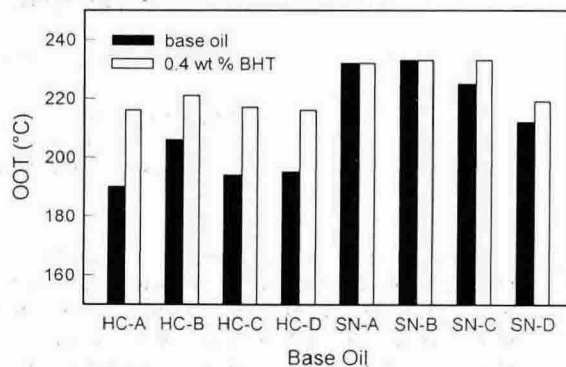


Fig. 4 Oxidation stability of some HC and SN oils

It is apparent from Fig. 4 that SN oils were, under the PDSC conditions, much more oxidatively stable than HC oils. Even after addition of BHT, oxidation stability of HC based oils was mostly lower than that of SN base oils. It does not correspond to a praxis experience that turbine oils based on HC oils are much more stable than those based on SN oils. That is most likely due to a high temperature character of oxidation as the OOTs were detected around 200 °C. Turbine oils are known as oils operating at low temperatures where a quite different oxidation mechanism occurs with respect to an oil composition [6]. Even incorporation of a 60 min. isothermal step at 150 °C (temperature of usual RBOT test) before detecting the OOT did not have a substantial effect on oxidation HC and SN oils.

4. CONCLUSION

PDSC is a very useful tool for evaluation of oxidation stability of lubricating oils. Small sample amount and analysis duration mostly up to 60 min are the main advantages. It is especially suitable for evaluation of high temperature oxidation. PDSC has a great potential for its utilization in the field of diagnostics of oil ageing and for a rapid assessment of oxidation stability of lubricating oils.

5. REFERENCES

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