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Oxidation Stability of Lubricants Measured by a PDSC Technique

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Abstract

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 purpose 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*

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 only be exploited 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 oxidising gas (oxygen, air) for analyses. 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 (such as temperature, oxygen pressure and flow rate) were evaluated and described elsewhere[2,3]. Analytical procedures for evaluation of oxidation stability of lubricating were also standardised 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 procedure 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.

This paper presents some results and experience with a PDSC analysis of fresh as well as operating motor oils, hydrocarbon base oils, and bio-diesel fuel. Effect of a low temperature antioxidant in different base oils has also been evaluated.

Experimental

Isothermal analysis according to ASTM D 6186

About 3 mg of a sample was weighed into a standard open Al pan and placed in the measuring cell. Temperature of the cell was increased from the ambient to the temperature of 200°C at a rate of 100°C/min and allowed to equilibrate for 2 min. After that period the cell was pressurized by oxygen to 3.5 MPa and the purge gas flow rate was adjusted at 100 ml/min. The oxidation induction time (OIT) was measured from the time the oxygen valve was opened. Detection of OIT was made by an extrapolation of the DSC signal when a strong exothermic reaction (oxidation) was 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).

Non-isothermal analysis ASTM E 2009

Again about 3 mg of a sample was prepared as in the previous method. Temperature was increased from ambient by the gradient of 10°C /min. Oxygen pressure was maintained at 3.5 MPa from the start of heating. Flow rate was adjusted to 50 ml/min. A similar signal to that in Fig. 1 was obtained and the oxidation onset temperature (OOT) was evaluated.

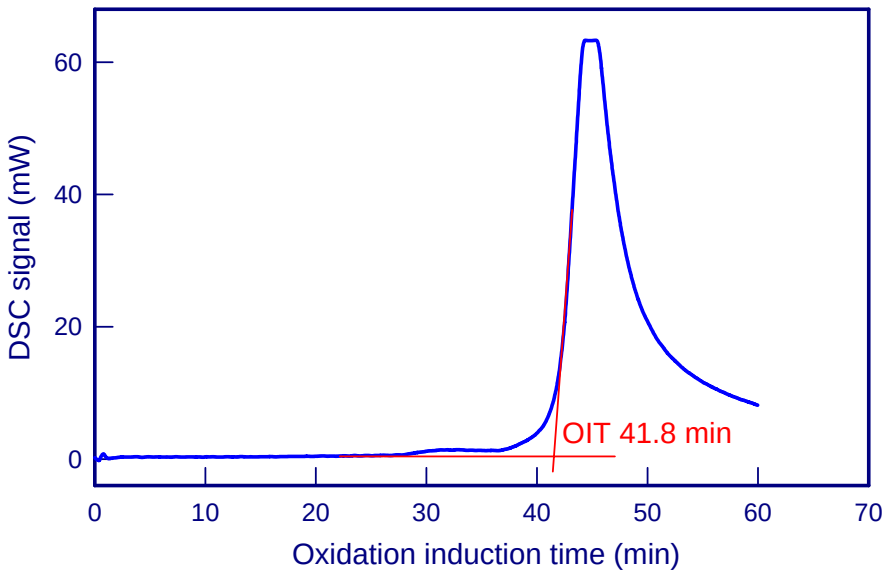

Figure 1 Pressure DSC analysis of engine oil

Results and Discussion

Motor oils

Engine oils were analysed by the isothermal procedure according to ASTM D 186. However, the temperature of PDSC analysis was decreased by 10 °C, which led to approximately doubled OIT`s (initial temperature recommended by the ASTM D 6186 is 210 °C). According our experience, temperature of 200 °C is more suitable for modern engine oils. Analysing more than 70 motor oils of different specifications and from different producers the OIT`s obtained were all in the range from 13 min to more than 120 min. This range allows very well differentiating between individual oils. OIT of most of the motor oils were from 30 min. to 50 min.

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 oxidised by a radical mechanism [4] 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 someway proportional to the antioxidant capacity of motor 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 OIT`s from PDSC analysis.

There were large differences between OIT`s of individual engine oils. Whereas oils with the European specification ACEA A3/B3,B4 had very good oxidation stability (with an extreme example of the Oil B), 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 D and E in Fig. 2).

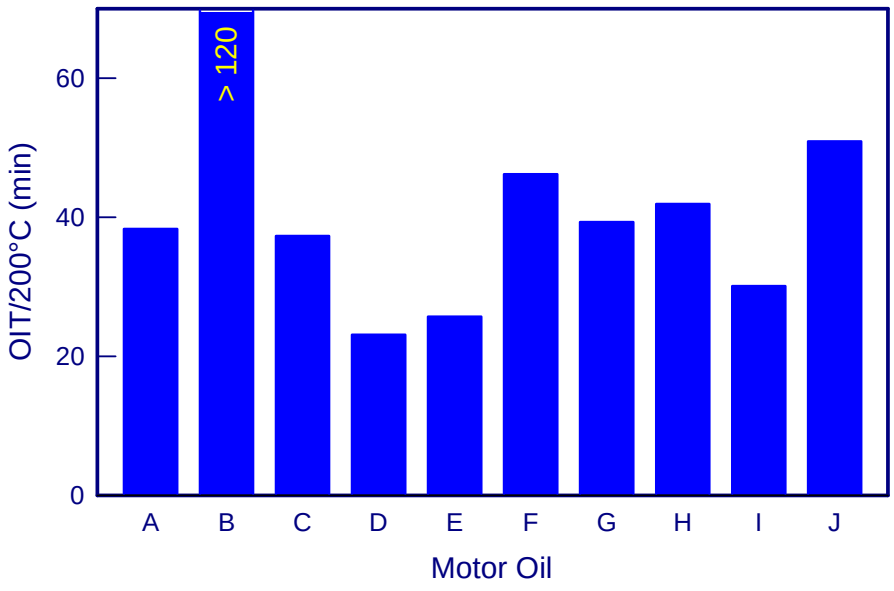

Figure 2 Oxidation stability of SAE 5W-30 motor oils by PDSC

Another example of PDSC utilization can be in the field of tribodiagnostics [5,6]. In Fig. 3 there is shown a decrease of OIT during operation of oil in a heavy-duty engine Volvo FH12. Drain interval of motor oil in the engine is 40 000 km, however, the oil was operated for up to 67 000 km. There is clearly an exponential decay of OIT`s showing that much of the antioxidant capacity of engine oil was consumed during the first 20 000 km. Moreover, another aspect in analysis of operating oils is very important. Operating and/or used motor oils should be analysed at a lower temperature. At a temperature of 200 °C the OIT`s obtained were too low especially in the final stage of the oil life. More appropriate results can be obtained analysing the oils at 180°C. Values of the OIT were about five times higher, and differences in OIT for neighbouring samples were quite recognizable even in the final stage of the oil life.

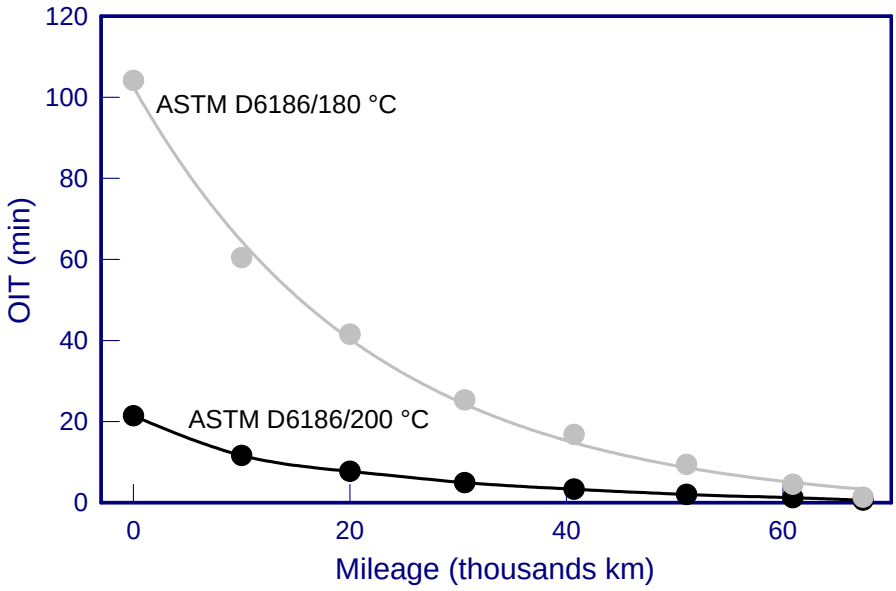

Figure 3 Decrease of OIT of motor oil during operation in a heavy-duty engine Volvo FH12

In the next Fig. 4 a similar plot is shown for motor oil operating in a personal car Škoda Octavia 1.9 TDi with a prolonged oil drain interval (up to 50 000 km). Depletion of antioxidant and lowering the oil antioxidation capacity during operation is there again clearly seen. Very interesting is also the effect of oil filling up on the antioxidation capacity that is clearly demonstrated by a PDSC analysis. Repeated addition of a fresh oil led to stabilising the antioxidation capacity of the operating motor oil. There are only a few alternatives in tribodiagnostics, if any, with such a clear response to a fresh oil addition as the PDSC analysis. The experiment is still in progress and samples of the motor oil will be collected up to the time of the car computer warning.

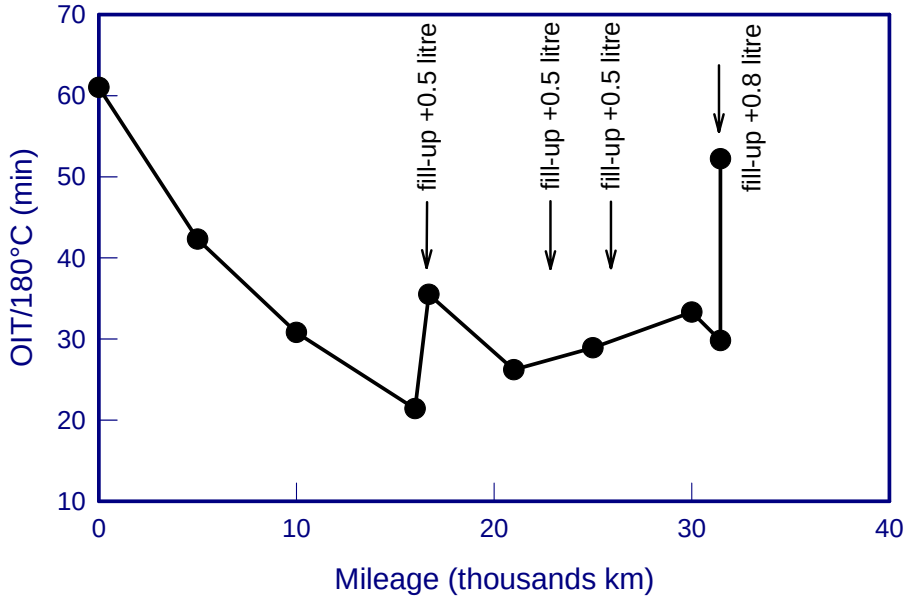

Figure 4 Decrease of OIT of motor oil during operation in a personal car Škoda Octavia 1.9 TDi (diesel fueled)

Base oils and hydrocarbon mixtures

Usage of an isothermic procedure is not the best choice for evaluation of oxidation stability of base oils. The OIT`s 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. A 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 OOT`s between 190^{o}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. 5, 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.

It is apparent from Fig. 5 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 OOT`s 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 [4]. 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.

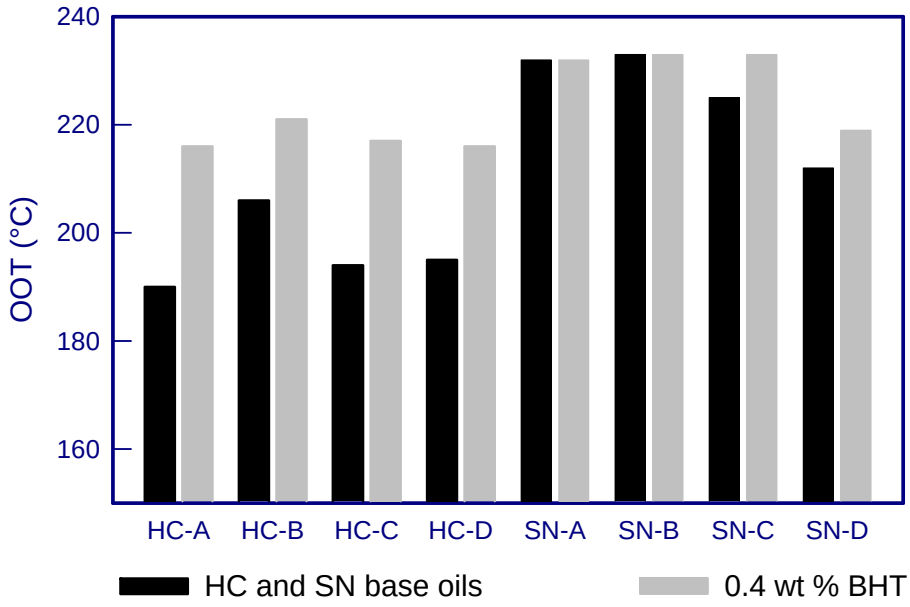

Figure 5 Oxidation stability of some HC and SN oils and effect of the BHT antioxidant

Another example for utilisation of a PDSC evaluation of oxidation stability of hydrocarbon and similar mixtures is shown in Fig. 6. Rape seed methyl esters were added to a conventional diesel fuels in different concentration up to 35 wt %. There is clearly seen a rapid decrease of oxidation stability of biodiesel while adding the first ten percent of RME into a conventional diesel fuel. Further increase of the RME concentration did not affect the oxidation stability of biodiesel as much as small percentage of RME.

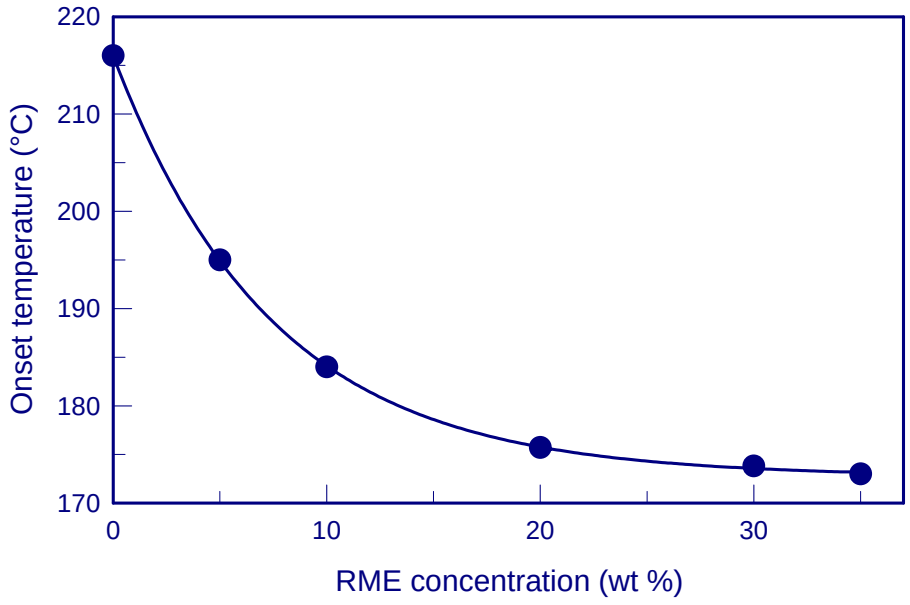

Figure 6 Oxidation stability of biodiesel fuel by PDSC technique

Conclusion

A pressure DSC 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 tribodiagnostics of oil ageing and for a rapid assessment of oxidation stability of lubricating oils and other hydrocarbon mixtures.

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