

A MULTI-SAMPLE HIGH-PRESSURE DTA FOR MEASURING OXIDATION INDUCTION TIMES

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ABSTRACT

This paper describes the design and operation of a DTA instrument which can run five samples simultaneously to measure their oxidation induction times in oxygen or air at pressures up to 70 bar (1000 lbf in⁻²) and isothermal temperatures up to 250 °C. The instrument may run five different samples to maximise productivity, or a given sample may be run in duplicate, triplicate, etc., to improve confidence in the result. Although designed for high-productivity testing of automotive lubricants, the instrument is applicable to other oxidation-inhibited materials such as greases, edible oils and polymers.

INTRODUCTION

Background

The useful lifetime of an automotive crankcase lubricating oil is limited by the effects of oxidation, and reasonable longevity requires the addition of an oxidation inhibitor. The inhibitor acts by combining with and stabilising radicals which are constantly being formed by thermo-oxidative reactions. When the inhibitor is depleted, the oil experiences rapid oxidation and its useful life is then over.

A major aim in formulating a new lubricant is to guarantee a minimum useful lifetime. High-pressure differential thermal analysis (HP-DTA) or high-pressure differential scanning calorimetry (HP-DSC) can be used as a bench-scale screening test for comparing the lifetimes of lubricating oils [1–4] and other products, such as greases [5], edible vegetable oils [6,7], and polymers [8], which contain oxidation inhibitors. The method usually involves maintaining a few milligrammes of the material at an elevated temperature so that the oxidation inhibitor is rapidly consumed, leading to a strongly exothermic reaction which is readily detectable by the instrument. The method is, therefore, an accelerated oxidation test and the time at which the exotherm appears is known as the oxidation induction time (OIT).

However, at the elevated temperatures needed to achieve reasonably short OITs (< 1 h), the hydrocarbons or additives in the oil (or other material) are volatile, so high pressures are essential to suppress any vaporisation which could lead to anomalous results. Air or O_2 at pressures up to 35 bar is routinely used, and an additional advantage is the enhanced reaction rate caused by the increased oxygen concentration: this allows the test to be performed at a lower temperature, which again helps to minimise vaporisation.

The important point about such HP-DTA or HP-DSC tests is that the OITs can correlate well with actual lifetimes if the experimental conditions are carefully chosen. The need for careful experimental design is well illustrated by the work of the National Bureau of Standards (NBS) on automotive crankcase lubricating oils [1,2]. The NBS showed that a good correlation needs the presence of ppm levels of metals such as lead, copper, tin, iron and manganese in the oil to simulate the presence of these metals in oil in an engine due to the wearing of components.

HP-DTA or HP-DSC is widely used in the petroleum industry, where it is regarded as a rapid, relatively inexpensive, and reasonably accurate technique for comparing the lifetimes of oils. Also, it uses only milligramme quantities of sample, which is a great advantage if only small amounts of some new formulation are available. Indeed, it was the considerable demand for such tests that motivated the development of the instrument described here.

The multi-sample concept

Several multi-sample ambient-pressure DTA instruments are described in the literature; for example, Howard [9] describes a six-sample DTA for measuring OITs for polymeric cable coatings in 1 bar oxygen. Also, Du Pont Instruments market a two-sample HP-DSC; however, the samples in that instrument are not isolated from each other, so gas-phase interaction is possible.

The apparatus described in this paper has been optimised for measuring OITs in air or O_2 at pressures up to 70 bar and isothermal temperatures up to $250^\circ C$ for five samples in a configuration which minimises any interactions.

DESIGN CONSIDERATIONS

Basic requirements

The starting point was a desire to have each of the five samples in an isolated chamber with its own atmosphere, uncontaminated by volatile

reaction products from another sample. This precaution eliminates any possibility of volatile oxidation products from one sample reacting with, and causing the premature oxidation of another. It was also considered desirable to have aluminium as the only metal in the vicinity of the sample, because aluminium is known to have minimal catalytic activity on any oxidation of oil in the vapour phase, which in turn may affect the liquid-phase oxidation.

Convection currents

Perhaps the greatest challenge in designing high pressure thermoanalytical apparatus is the need to minimise convection currents, which become more severe at higher pressures. Convection currents develop in a fluid wherever there is a temperature gradient, and their effect in DTA is to create noise and drift on the ΔT signal. However, there are two remedies for convection currents: minimise the temperature gradient, and restrict the vertical flow of gas. Both options are used in this design as described below.

Engineering constraints

A major challenge in designing the present instrument was one of engineering. On the one hand, seven thermocouples, two power leads and two gas lines must enter the system; on the other, the size of the furnace must not exceed certain limits, otherwise the performance of the instrument is impaired. Specifically, the diameter of the furnace should be no larger than that required to accommodate the samples, because any increase in diameter is at the expense of increased temperature gradients across the furnace, which in turn leads to drift in the heat flux signal. This restriction and other considerations led to the choice of 1 mm o.d. mineral-insulated metal-sheathed thermocouples for temperature measurement. These have several clear advantages: (a) they can pass through the pressure vessel wall via standard fittings; (b) the wires inside are continuous from the junction to the amplifier terminals, thereby avoiding any spurious voltages at intermediate connections; (c) the wires are protected from high-temperature high-pressure corrosion by the Inconel sheathing; (d) the aluminium platform for the sample pan (Figure 3) can sit on the tip of the sheath with good thermal contact.

DESCRIPTION OF APPARATUS

The furnace and pressure vessel

A cross section of the pressure vessel is shown in Fig. 1. At its core is an aluminium furnace (1) with six symmetrically-spaced cylindrical chambers (2) as shown in top view in Fig. 2. Each chamber contains a 1 mm o.d.

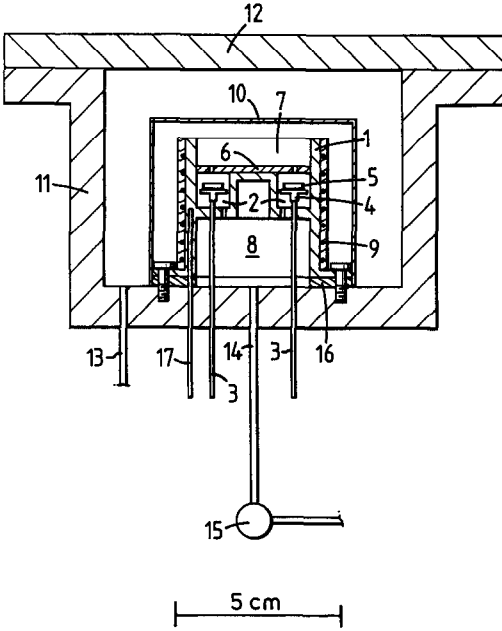


Fig. 1. A section through the pressure vessel.

mineral-insulated metal-sheathed type K thermocouple (3) with an aluminium platform (4) to support the sample pan (5). One platform supports an empty pan (the reference), and the other five support pans with samples. A platform is shown in more detail in Fig. 3. A lid (6) 2 mm thick covers the chambers and makes good contact with the furnace. The role of the lid is to reduce convection currents by minimising temperature gradients within each chamber and by acting as a barrier to convective gas flow. Parts (7) and (8) are empty chambers in the aluminium block.

The furnace is heated by a 100 W Nichrome resistance winding (9) insulated electrically from the furnace by silica tape and surrounded by alumina cement. A stainless steel inverted cup (10) surrounds the furnace and acts as a heat shield by containing convection currents. A layer of

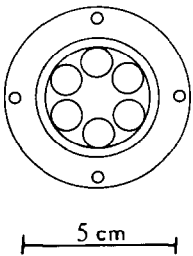


Fig. 2. A top view of the aluminium furnace block.

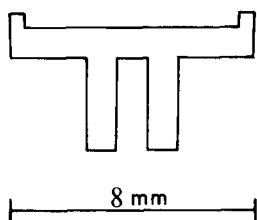


Fig. 3. A section through a sample platform.

alumina wool (not shown) in aluminium foil in the cup just above the furnace provides additional insulation. The base of the furnace is in the form of a flange (Fig. 2) and is screwed to the base of the pressure vessel with a gasket (16) in between. This gasket has two roles: to act as a resistance to heat loss from furnace to pressure vessel, and to provide a gas seal to ensure the gas flow pattern described below. A 1 mm o.d. thermocouple (17) in the furnace wall acts as a sensor for the furnace temperature programmer.

The pressure vessel (11) is of conventional design with the lid (12) secured by thumb-tight bolts and sealed under pressure by a self-sealing O-ring. The six thermocouples (3), the sensor thermocouple (17), and the gas inlet (13) and outlet (14) enter the vessel via compression fittings which screw into the base of the vessel. The power leads (not shown), enter by ceramic-insulated fittings which are silver soldered into the base of the vessel.

Gas flow arrangement

The gas pressure is set by a regulator and the gas fills the system by entering inlet (13), passing down through each of the six holes in the lid (6), through each chamber (2), into chamber (8) via 1 mm holes in the bottom of each chamber, then down the outlet (14) to needle valve (15) which is set to control the flowrate. When a static atmosphere is required, valve (15) is closed and a valve (not shown) near the regulator is opened to give a bleed of approximately 200 ml min^{-1} . This bleed is essential otherwise the expansion of the gas as the furnace is heated to set-point will give a significant pressure rise.

Temperature control

Furnace temperature is controlled by a Control and Readout Limited CRL455 programmer capable of a nine-ramp, nine-dwell sequence. The mains a.c. supply is stepped down to 40 V a.c. using a transformer and switched by a solid-state relay. Although OITs are measured at a constant temperature, better repeatability is achieved if that temperature is reached by a controlled ramp rather than by uncontrolled heating. Details of the

programme are given below. Another essential feature of the CRL455, is that it has so-called PID control; in effect, it reaches set-point with minimal overshoot and maintains it to within $\pm 0.1^\circ\text{C}$ indefinitely. In contrast, a P-only controller never reaches the set-point but stabilises below it with an error which depends on ambient temperature. The temperature is calibrated using indium at 1°C min^{-1} .

DATA COLLECTION, DISPLAY AND ANALYSIS

The six thermocouples (3) are interconnected so that five signals are produced each of which corresponds to the temperature difference ΔT between a thermocouple and the reference thermocouple. Given the radial symmetry of the furnace, this is the only logical arrangement to obtain ΔT signals which should be theoretically zero. Each of these signals passes to an amplifier (gain 10 000) and an A-to-D converter, and all five are sent down an RS232 (serial) line to a personal computer (PC). The amplification, conversion, and multiplexing are achieved using a Linseis 8500 unit which is configured to give 1000 counts for a full-scale input of $100\ \mu\text{V}$.

The PC is loaded with customised software for data collection and analysis, and during the run it provides a real-time colour-graphics display of the five signals. After the run each curve is called up onto the screen for the operator to define a baseline. Thereafter, the curve is analysed automatically to give the oxidation induction time and the peak time. The oxidation induction time is calculated by the computer as the time at which the signal is 5% of the peak height.

OPERATION

Procedure

As mentioned above, the test conditions are based on those devised by the NBS. A catalyst consisting of chelated metal ions dissolved in white oil is used to simulate the catalytic effect of metal ions resulting from the wearing of engine components. The metal concentrations used are those given in ref. 2.

The test sample is prepared by pipetting 1 ml of the oil (a fully-formulated automotive lubricant) into a 10 ml glass bottle and adding, by pipette, $30\ \mu\text{l}$ of the liquid catalyst. The components are then mixed on a vibrator. A length of platinum wire (approximately 0.2 mm diameter) is used to transfer drops of mixture onto a disposable aluminium sample pan of type described below, to achieve a mass of $1.5 \pm 0.1\ \text{mg}$. The five samples are then loaded into the instrument, which is normally maintained at

100 °C. The vessel is closed and pressurised to 35 bar with pure oxygen, with no flow through the furnace, but with a 200 ml min⁻¹ bleed of gas to stabilise the pressure as described above. The following temperature programme is then applied: 100 °C to 150 °C at 10 °C min⁻¹; 150 °C to 175 °C at 5 °C min⁻¹. Such a programme ensures a repeatable approach to set-point, with an overshoot of less than 0.2 °C.

PERFORMANCE

Repeatability within a run was assessed by running five samples of a given oil. The oil is a fully-formulated standard against which the performance of other oils are compared. Typical DTA curves are shown in Fig. 4. Such experiments with five samples of the standard oil are run frequently to confirm its OIT, and the range of OITs within a run is typically ± 45 s. Examination of the results also confirmed that there is no correlation between OIT and sample position; this implies the positions are effectively identical with no asymmetry.

If the mean OIT for a run is followed over a period of weeks, the range is ± 1 min; while over a period of months, the mean shows a gradual drift of a few minutes. However, this does not pose a problem since all measurements are compared to the standard oil, which is run every few days. It must also be noted that OIT measurements for some oils show a repeatability within

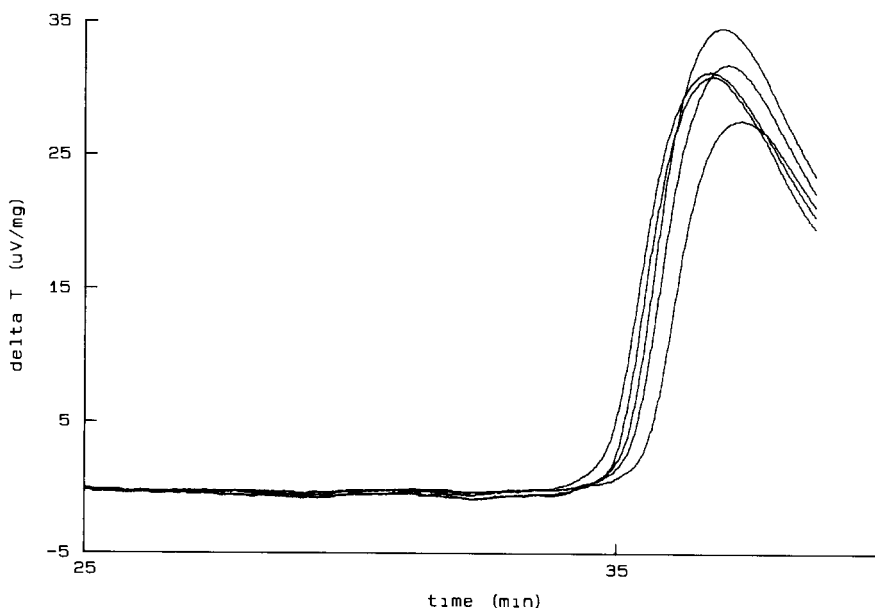


Fig. 4. DTA curves for five samples of an oil run using the NBS conditions.

and between runs of as much as ± 3 min. Such problematic oils are, however, rarely encountered.

FACTORS WHICH AFFECT THE MEASUREMENTS

Temperature, pressure and catalyst level

Some experiments were run to quantify roughly the role of the experimental variables, with the following results: a $+0.4^{\circ}\text{C}$ error in temperature gives a -1 min error in OIT; a $+1$ bar error in pressure gives a -1 min error in OIT; and a $+3 \mu\text{l}$ error in added liquid catalyst gives a -1 min error in OIT.

Type of sample pan

Of the two types of disposable aluminium pan shown in Fig. 5, the curved one gives much better repeatability in OITs. The reason for this becomes apparent when the pans are examined after a run: the oil accumulates beside the inner wall but does so more evenly in the curved pans because of their less angular shape. OIT measurements, whether by DSC or some other technique, are notoriously sensitive to such factors.

Interactions between samples

As mentioned above the instrument was designed to minimise any interactions between the samples via the gas phase, and this was verified as follows. Five samples of oil A were run and the mean OIT was 12 min; five samples of oil B were run and the mean OIT was 55 min. Then 3 samples of oil A were run simultaneously with 2 samples of oil B; oil A had an OIT of 12 min and oil B 55 min. The conclusion was that, for these oils at least, no interaction was occurring.

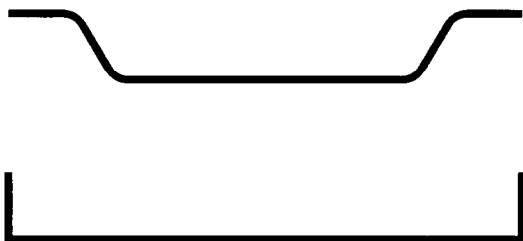


Fig. 5. Two types of 6 mm o.d. aluminium sample pan. The pan with curved sides gives more repeatable results.

CONCLUSION

The instrument described here has been applied to the measurement of OITs for automotive crankcase lubricants and has led to substantial increases in accuracy and productivity. Clearly, similar improvements could be achieved for OIT measurements on other materials.

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