

DESCRIPTION OF THE O₂ PRESSURE INFLUENCE ON THE OXIDATION TIME OF MOTOR OILS

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A characteristic index for the oxidation stability this is the oxidation induction time (OIT) which is defined by the time between the start of oxygen exposure and the onset of oxidation. Pressure DSC is required to increase oxygen concentration in order to achieve faster reactions at lower temperatures. OIT measurements of reference engine oils have been used to study the influence of oxygen pressure in the range from 0.1 to 10 MPa. A power law relationship was derived to describe this correlation between OIT and oxygen pressure. From this a quantitation factor is proposed to represent the influence of stabilizer. The exponent describes the sensitivity of the oxidation reaction of the oil towards the oxygen pressure and the term ‘inherent stability’ is proposed for that. This relationship characterizes in more details the oxidation behavior. Extrapolation to higher pressures indicates, that the stabilization effects of additives can be overcome by the inherent stability. This signifies, that the ranking of the oils can be affected by the oxygen pressure.

Keywords: engine oils, oxidation induction time (OIT), oxidation stability, oxygen pressure influence

Introduction

The determination of the stability of motor oils is one of the key issues in reliable ranking of the quality. Real time engine test cost about US\$ 30,000 each and there were 18–20 engine tests to qualify these oils. Therefore, a fast screening tool is required to rate oils regarding oxidation stability. In this investigation oxidation induction times and temperatures measured to characterize reference engine oils.

The measurement of the oxidation induction time (OIT) is a fast and standardized method to characterize the stability of organic materials like polymers and oils against oxygen attack [1]. This accelerated aging test is performed isothermally at elevated temperature (typically between 150 and 210°C) in an oxygen containing atmosphere. The time from first oxygen exposure until the onset of oxidation is the OIT value. Modern synthetic oils with anti-oxidative additives are designed to withstand higher temperatures and longer exposure times than common mineral oil. In such cases, pressure DSC is required to shorten analysis time by increasing oxygen concentration for faster reactions at lower temperatures and to suppress evaporation of volatile components. The optimal temperature and time frame for the OIT measurements have to carefully be optimized so that even small differences in stability can be identified. Influences of sample preparation, experimental parameters and measurement techniques are described in [2]. The influence of temperature at elevated oxygen pressure has been discussed in [3]. In this paper an analysis of the pressure dependence of OIT is given, based on a kinetic approach.

Faster testing can be achieved using the oxygen onset temperature method (OOT, [4]) where the start temperature of oxidation during heating is measured by DSC. The increase of O₂ pressure reduces the onset temperature. But, differentiation of materials can be assessed by the OOT method only if the stabilities of the materials are not too close to each other, because the onset temperatures may be too close if usual heating rates of 10 K min⁻¹ are used. Kopsch [5] describes the decomposition of lubricating oils and additives using the peak temperatures of the dynamic DSC curves, and low temperature oxidation of fuels were characterized at various pressures using kinetic parameters derived from Arrhenius equation. A car engine test of a lubricating oil showed how the thermal stabilities measured by TG and DSC were changing during the usage period [6].

The following study also deals with the ranking of reference engine oils with respect to oxidation stability. The influence of the oxygen pressure on the OIT was determined to check if the ranking is affected by that. A relationship between OIT and O₂ pressure should allow for a better comparison of various oils.

Estimation of the oxygen pressure dependence of OIT

If all the molecules reacting together are in the sample the reaction kinetics can be described by

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

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where α is the conversion, k is the temperature dependent rate constant and $f(\alpha)$ is the conversion function. Normally, the temperature dependence of k is described by an Arrhenius-equation. For $f(\alpha)$ several different approaches are used [7]. For instance, the conversion function is $f(\alpha) = (1-\alpha)^n$ for a n^{th} -order reaction. In the case of the oxidation reaction the oil acquires oxygen by diffusion. An inhibitor may react with oxygen and reduces the O_2 activity for the oil oxidation. This should be considered by a modified equation, e.g.

$$\frac{d\alpha}{dt} k(T)f(\alpha)f_o(c_{O_2}(t)) \quad (2)$$

where $c_{O_2}(t)$ is the time dependent O_2 concentration and f_o is the accelerating function due to the oxygen concentration in the sample. Equation (2) is a very strong simplification, and can not hold for an overall description of the reaction kinetics. However, in the present situation we are interested in the OIT, t_{OIT} . Thus, the kinetics is only discussed for very small conversion and relative short times. For this purpose Eq. (2) may be sufficiently precise. For small conversions the following approximations are used: $f(\alpha \rightarrow 0) = 1$ and $f_o(c_{O_2}(t \rightarrow 0)) = k_c c_{O_2}^n(t)$, as a normal n^{th} -order approach. As a consequence of these conditions Eq. (2) becomes n^{th} -order relating the reaction rate to the oxygen concentration:

$$\left. \frac{d\alpha}{dt} \right|_{\alpha \rightarrow 0} = k(T)k_c c_{O_2}^n(t) \quad (3)$$

In the next step, the time dependence of c_{O_2} has to be estimated. An oxygen generation process, diffusion, and a consumption process, e.g. a reaction with the inhibitor, occurs. For the O_2 concentration follows

$$\frac{dc_{O_2}}{dt} = Dg(c_e - c_{O_2}) - r_i(c_{O_2}) \quad (4)$$

where c_e is the equilibrium O_2 concentration, D is the diffusion coefficient between O_2 gas and oil, g is a geometry factor and r_i describes the reaction rate of the inhibitor with oxygen. In the case where the consumption reaction follows n^{th} order the rate is $r_i = k_i c_{O_2}^n$. In the case of first order, the time dependence of the concentration is

$$c_{O_2}(t) = c_e A_c (1 - \exp(-b_c t)) \quad (5)$$

where $b_c = gD + k_i$ and $A_c = gD/b_c$.

If the loss of antioxidants due to evaporation is taken into account in r_i , the $c_{O_2}(t)$ gets a structure like Eq. (5). However, the parameters b_c and A_c are now dependent on the concentration of the inhibitor concentration c_i .

A more general approach for c_{O_2} could be the Avrami equation

$$c_{O_2}(t) = c_e A_c (1 - \exp(-b_c t^m)) \quad (6)$$

which describes the delay of the O_2 concentration increase due to the inhibitor reaction at the begin of the oxidation. Simulations of the reaction behavior using Eqs (5) and (6) in Eq. (2) show that both functions for $c_{O_2}(t)$ deliver a fast reaction after an induction period in which the oxidation is practically not present.

For the discussion of OIT, $c_{O_2}(t)$ is only relevant in the initial time range ($t \rightarrow 0$). It follows from Eqs (5) and (6) that

$$c_{O_2}(t \rightarrow 0) = c_e A_c b_c t^m \quad (7)$$

with $m = 1, 2, 3$ for example.

Introducing Eq. (7) in (3) describes the rate at the beginning by

$$\frac{d\alpha}{dt} = k k_c (A_c b_c)^n c_e^n t^{mn} \quad (8)$$

Integration of Eq. (8)

$$\int_0^{\alpha_{OIT}} d\alpha = k k_c (A_c b_c)^n c_e^n \int_0^{t_{OIT}} t^{mn} dt \quad (9)$$

delivers an expression for t_{OIT} :

$$t_{OIT} = A_1 c_e^{-\frac{n}{mn+1}} \quad (10)$$

where $A_1 = ((nm+1)\alpha_{OIT} k^{-1} k_c^{-1} (A_c b_c)^{-n})^{1/(nm+1)}$

To get the relation between OIT and the partial oxygen pressure, p , Henry's law is used to describe the pressure dependence of the equilibrium concentration c_e .

$$p = K_H c_e \quad (11)$$

where K_H is Henry's law constant. Finally, the combination of Eqs (10) and (11) describes the oxygen pressure dependence of the OIT as a power law:

$$t_{OIT} = A p^{-q} \quad (12)$$

where $A = A_1 K_H$ and $q = n/(mn+1)$.

The pre-factor A mainly depends on the diffusion coefficient, the rate constants of the oxidation reaction on the reaction of the inhibitor and the inhibitor concentration. We suggest to define this factor as a measure of the 'quantity of oxidation resistance' of the oil. The exponent p represents the slope in an double logarithmic $\log t_{OIT} - \log p$ diagram. If we set $m=1$, q is only influenced by the order of the oxygen consumption reaction, Eq. (3), and this parameter is between 1 and 0.5. If we allow for m to be larger ($m>1$) it follows that $0 \leq q \leq 1$. For $q=0$, the oxidation is pressure independent. In such a case oxygen does not play an important role for the reaction. This is a fundamental discrepancy, nevertheless we can conclude that a smaller value for q indicates a larger oxygen resistance behavior which may be called 'inherent oxida-

tion stability'. At $q=1$, every oxygen molecule react with the oil. In this sense q describes the quality of the oxygen resistance of the oil. A higher q indicates a higher oxygen sensitivity.

Experimental

The following motor oils were investigated: SP287 (1006-2), SP288 (1008-1) and SP289 (443-1) from ASTM TEST Monitoring Center, Pittsburgh PA. SP289 and SP288 passed a number of Engine Tests Sequence IIIG with an average of 35 and 125% viscosity increase. SP287 failed the tests with an average of 245% viscosity increase.

The OIT and OOT were measured according to the ASTM standards using samples of 3.0 to 3.3 mg mass in open aluminum pans at 3.5 MPa pure oxygen pressure [1, 4].

A Mettler Toledo STAR^e system with HP DSC827^e was used to apply pressure during the DSC measurements. The oxygen pressure was set at room temperature before starting the heating program. An oxygen purge gas flow through the measuring cell was established using a mass flow controller giving a flow rate of 50 mL min⁻¹ at ambient pressure. The pressure was kept constant during the measurement using an electronic pressure controller. The OIT method used the following temperature program: heating from 35 to 195°C at a rate of 40 K min⁻¹ followed by isothermal holding at 195°C until the oxidation peak was detected. The measurements were stopped automatically if the DSC signal reached a value of 8 mW and a delay time of 1 min was added. The OOT method used a linear heating from 35 to 300°C.

Results

Isothermal measurements (OIT)

The isothermal measurements of the oxidation stability (OIT) show a clear ranking of the oils, as the Fig. 1 indicates. This corresponds to the ranking by the engine tests where the SP289 is the most stable one. But, the oil SP287 did not show a normal steep onset of oxidation but only a small exothermic peak after about 20 min. No further oxidation was shown even after 10 h measurement time. This behavior would give difficulties in routine analysis where the DSC signals must be bigger than 3 mW [1].

As it could be expected from Eq. (12), the increase in pressure reduces the OIT dramatically (Fig. 2). As a consequence the differentiation of various oils can get more difficult if the times are too short if selecting the temperature too high.

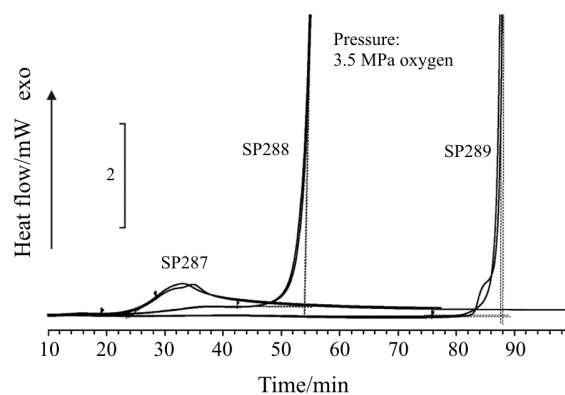


Fig. 1 OIT of three reference engine oils. 3.5 MPa O₂ pressure, 35 to 195°C at 40 K min⁻¹ followed by isothermal holding at 195°C

The reproducibility of the OIT determination was checked repeating the measurement five times for each sample at different pressures. The variation of the OIT values always were smaller than 3 min.

The relationship between the OIT and pressure is given in Fig. 3, considering the data shown in Fig. 2 for one oil and similar measurements of the other oils. The oil SP287 behaves differently than the other oils and shows only a small oxidation peak (Fig. 1). Therefore, the peak temperature was also determined and described in Fig. 3. As a consequence of Eq. (12), the data should show a linear relationship in the $\log t_{\text{OIT}} - \log p$ diagram. Figure 3 shows the good agreement between the theoretical equation and the experimental data. Fitting the measuring data according to Eq. (12) a set of parameters A and q are calculated for each oil (Table 1).

The OIT at ambient pressure and at lower oxygen concentration (low partial pressure) can be estimated using these parameters. At and high pressure of approx. 28 MPa the higher stable oils SP288 and SP289 have the same OIT of approx. 20 min. Beyond 28 MPa, the SP288 seems to be more stable than SP289, a fact which could be interpreted by the higher inherent stability of the oil against oxidation. At the same high pressure of approx. 26 MPa, the SP287 would show a so fast reaction of approx. 9 min that the onset and peak time are approximately the same. The parameters A (Table 1) clearly differentiate the oils in terms of quantity of O₂ resistance. But, the q

Table 1 Fit parameters according Eq. (12) for the data given in Fig. 3

	$A/\text{min (MPa)}^q$	q
SP287 onset	48.21	0.514
SP287 peak	76.71	0.659
SP288 onset	90.69	0.447
SP289 onset	163.10	0.622

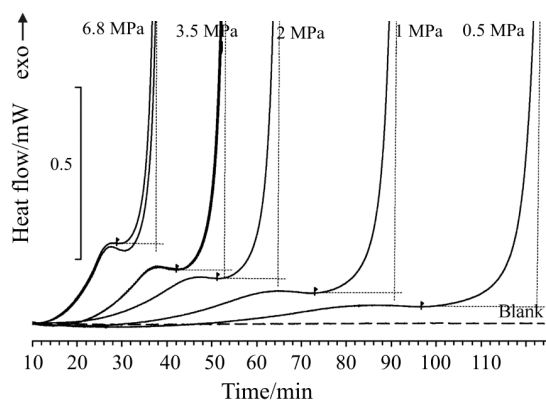


Fig. 2 OIT measurements of SP288 reference engine oil at various O_2 pressures. DSC method: 35 to 195°C at 40 K min^{-1} followed by isothermal holding at 195°C

terms show that oil SP288 has a so-called higher inherent oxidation stability. With q being as low as 0.44 this oil is much less sensitive to a change in O_2 pressure. It can be assumed that the reaction order n for oil SP289 is $n \approx 2$ and for SP287 $n \approx 1$, both with $m \approx 1$. But for SP288: $m > 1$ and $n \approx 1$.

All oxidation reactions of the oils measured show a small exothermic reaction before the main strong oxidation starts (Figs 2 and 3). These reactions are also influenced by pressure, i.e. the peak or shoulder is reached faster at high pressure. This may be interpreted as the re-

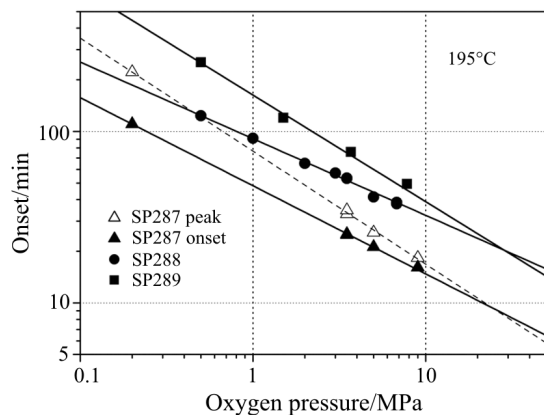


Fig. 3 Correlation of OIT with oxygen pressure for the three reference engine oils, measured at 195°C. The lines represent the linear relationship according to Eq. (12)

action of the anti-oxidant and could also be used to characterize such additives. But this behavior gives some problems in the onset determination for the OIT. Especially if the main reaction is weak and the respective slope of the inflection tangent is not so steep, a significant shift in the results would follow.

Dynamic measurements (OOT)

Faster testing can be achieved if the oxidation onset temperature (OOT), that is the start temperature of oxidation, T_{OOT} , during heating is measured by DSC. The results of the fast OOT measurements at ambient and 3.5 MPa pure oxygen pressure are summarized in Table 2. The three oils are clearly differentiated for their stability against oxygen attack and show the same ranking as the engine tests. The most stable sample is SP289 with an OOT of 253°C. The least stable oil, SP287, shows an OOT of 232°C only. The measurements at 0.1 MPa showed the same ranking, but the results were more scattered. The standard deviations of the OOT results at 0.1 MPa are more than 10 times bigger than the standard deviations of the OOT at 3.5 MPa oxygen pressure. As a conclusion, OOT measurements require an increased oxygen pressure for better reproducibility.

Conclusions

OIT makes a fast pre-selection possible of candidate anti-oxidants in various base oils. Measurements at ambient pressures need high temperatures to get reasonable OIT values which could lead to evaporations. The OIT determination at elevated oxygen pressure proved to be highly reproducible with good ranking capabilities.

The O_2 pressure dependence of t_{OIT} follows a power law. The resulting parameters allow a more detailed understanding of the reaction condition related to oxidation stability. Extrapolation to very high oxygen pressures indicates that the less stable oil SP288 would be inherently more stable than the SP289. OIT measurements at different pressures show the influ-

Table 2 Oxidation onset temperatures at two oxygen pressures, measured at 10 K min^{-1}

Measurement	$T_{OOT}/^{\circ}\text{C}$ at 0.1 MPa			$T_{OOT}/^{\circ}\text{C}$ at 3.5 MPa		
	SP287	SP288	SP289	SP287	SP288	SP289
1	265.3	280.5	281.0	232.2	249.5	252.7
2	262.9	271.9	285.2	232.1	249.1	252.8
3	263.9	274.6	282.6	232.0	249.5	253.1
Mean/ $^{\circ}\text{C}$	264.0	275.7	282.9	232.1	249.4	252.9
Std. deviation/ $^{\circ}\text{C}$	1.21	4.40	2.12	0.10	0.23	0.21

ence of the stabilizer on the autoacceleration reaction before the main oxidation starts.

Fast cooling times (approx. 14 min) of the high pressure DSC used do not extend the experimental time in comparison to the often used measurements at ambient pressure. OIT gives better differentiation and reproducibility compared to OOT, but needs up to 100 min, typically.

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References

- 1 ASTM E 1858-00, Standard Test Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry, American Society for Testing and Materials, West Conshohocken, PA.
- 2 R. Truttmann, K. Schiano and R. Riesen, Oxidative induction time determinations of polyethylenes, Influences of temperature, pressure and crucible material on the results, in: T. Riga, G. H. Patterson (Eds), ASTM STP 1326, Oxidative Behavior of Materials by Thermal Analytical Techniques, American Society for Testing and Materials, 1997, p. 184.
- 3 S. M. Marcus and R. L. Blaine, Estimation of bias in the oxidative induction time measurement by pressure DSC, in: T. Riga, G. H. Patterson (Eds), ASTM STP 1326, Oxidative Behavior of Materials by Thermal Analytical Techniques, American Society for Testing and Materials, 1997, p. 172.
- 4 ASTM E 2009-99, Standard Test Method for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry, American Society for Testing and Materials, West Conshohocken, PA.
- 5 H. Kopsch, Thermal Methods in Petroleum Analysis, VCH, Weinheim 1995.
- 6 Ö. Karacan, M.V. Kök and U. Karaaslan, Dependence of Thermal Stability of an Engine Lubricating Oil on Usage Period, JTAC 55 (1999) p. 109.
- 7 M. E. Brown, Introduction to thermal analysis, Chapman and Hall, New York 1988, p. 128ff.

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