

Development of a new oxidation stability test method for lubricating oils using high-pressure differential scanning calorimetry

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Abstract

There is an industry-wide need for a rapid oxidation bench test that can be used to establish the oxidation stability of engine oils, greases, transmission and hydraulic fluids, turbine oils and vegetable oils. The oxidation stability of lubricants as estimated by high-pressure differential scanning calorimeter (PDSC) has long been of interest to the thermal science community. A group of industrial lubricating oils were used to establish a relationship between certain standard variables and oxidation induction times (OITs) by PDSC. The variables studied were temperature, pressure, heating rate, sample mass, sample pan types, soluble catalyst concentration and gas flow rate. Several oxidation induction time methods were developed to rank a series of lubricating oils. These results correlated well with an oxidation stability test (ASTM D943) used widely to characterize industrial oils. The new method is rapid, employs a soluble metal catalyst and requires only microliter samples for testing with good precision.

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1. Introduction

Fundamental knowledge of the oxidative properties of lubricants is necessary to predict the long-term thermal stability of these fluids, which is a critically important lubricant property. Oxidation properties evaluated experimentally are often used to predict actual lubricant service life in high temperature and other extreme applications. The more resistant a lubricant is to oxidation, the less tendency it has to form deposits, sludge, and corrosive byproducts in grease, engine

oil and industrial oil applications. It is also more resistant to undesirable viscosity increases during use. Igarashi [1] has discussed various chemical reaction mechanisms based on free radicals which are thought to be involved in the oxidative degradation of engine oils. Many studies have described how the molecular composition of base oil influences its physical and chemical properties, especially its oxidation stability [2–8]. In general, oils high in polynuclear aromatic content and certain sulfur and nitrogen containing species exhibit faster oxidation. The ASTM D943 test method is very widely used in industry to assess storage and long-term service oxidation stability of inhibited steam-turbine oils in the presence of oxygen, water, copper and iron at an elevated temperature

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(95 °C). This method is also used for testing hydraulic and circulating oils having a specific gravity less than of water and containing rust and oxidation inhibitors. Unfortunately, however, this test method takes a long time to complete (>1 year in some cases).

In developing new lubricants, it is not usually possible to screen a large number of base oils and anti-oxidant treat level combinations by running expensive and time-consuming performance tests using mechanical hardware. For these reasons, it has become necessary to seek development of new oxidation stability tests, which are capable of representing field performance within a short testing time. The trend is now to simulate the oxidation of fully-formulated lubricating oil more closely in laboratory bench tests like following: the Penn State Microreactor [9]; thin-film oxygen absorption test using a standard rotary bomb oxidation test apparatus [10]; bulk oil oxidation test based on ASTM D943 [11]; modified open test tube type of apparatus under conditions that simulate those encountered in the internal combustion engines [12]; peroxide accumulation and determination of oxidation induction time (OIT) using methods such as the rotary bomb oxidation test (RBOT; ASTM D2272), pressure DSC as well as the Institute of Petroleum IP48 test and FTIR analysis [13].

Significant advances in analytical instrumentation have given a big boost to the process of developing new lubricants. For example, inverse gas chromatography has been utilized to monitor the oxidation stability of lubricating oils, by passing test fluids over oil-coated chromosorb packed in a GC column and measuring the retention index to monitor oil degradation. This technique compared well with PDSC data [14]. Improvements in thermal analysis hardware and methods are a prime example of the changes that allow rapid assessment of base stocks, additives and finished lubricants while reducing the number of expensive full-scale tests. A primary tool employed to determine the oxidation of lubricants is differential scanning calorimetry (DSC) or high-pressure DSC (PDSC) where oxygen concentration is adjusted to exceed that at ambient pressure to expedite the oxidation process. In DSC, oxidative and thermal stability is evaluated by observing “thermal events” that result in a differential heat flow between the sample and reference pans of the calorimeter. DSC is typically used to measure OIT, which measures the time interval to

the onset of exothermic oxidation for a material at a specified temperature in an aerobic atmosphere and is the period of time during which the oxidation rate accelerates from zero to a maximum. The onset of oxidation is signaled by an abrupt increase in the sample’s evolved heat. The OIT is commonly used because of its relative ease and speed. DSC has been successfully used to predict the anti-oxidant degradation times for lubricants under simulated engine conditions [15].

OIT measurements using PDSC offer two main benefits. First, high-pressure decreases sample volatility by elevating boiling points, and second, it increases the concentration of the reacting gases as discussed above. This allows use of lower test temperatures or shorter test times at the same temperatures. The remaining useful life of lubricants evaluated using a PDSC technique were shown to be more accurate than the results obtained using DSC and it enabled the US Air Force to reduce material and labor costs by eliminating scheduled oil changes [16]. In preliminary investigations, numerous PDSC methods have been developed to determine the oxidation stability of synthetic [17,18], mineral [19–25] and vegetable oil based engine oils [26–29], metal working and hydraulic fluids [30] and greases [31]. A standard ASTM method D6186-98 is also available to determine oxidation induction time of lubricating oils using PDSC. Initially, Walker and Tsang [19] tried to compare engine tests and DSC measurements and concluded that a test for oxidation stability should not necessarily display an exact correlation with an engine test, which represents an integration of many operational factors. Rhee [31] also concluded that there is no direct relationship between PDSC results and ASTM D942 (for determining oxidation stability of grease by a bomb test) and ascribed this to a variation of pressure in the bomb test, which might be giving misleading indications as to the oxidation of grease. Nakanishi et al. [32] studied the oxidation stability of synthetic lubricants with a corrosion and oxidation stability test (COST), pressure DSC and hydroperoxide titration tests (HPT), but they found no correlation between the induction time in PDSC and the total acid number (TAN) and viscosity increase in the COST. To establish a correlation between PDSC results and oxidation stability test data, close simulation of engine test or D943 conditions in PDSC tests is required. This has been accomplished by Hsu et al. [33], by including soluble metal

catalysts along with a synthetic oxidized high-boiling gasoline fraction (synthetic piston ring “blow by”) to test oxidation stability of crankcase lubricants (eight ASTM Sequence IIID high temperature engine test reference oils). It was found that PDSC results correlated well with the viscosity increases of reference oils as determined by engine tests. In other studies, the base oil composition in terms of 16 hydrocarbon species, defined using column chromatography and mass spectrometry, has been used for correlation to the long-term turbine oil bench oxidation test (ASTM D943) or gasoline engine tests (Sequence IIIE and VE) by Stipanovic and coworkers [34–36]. This approach has met with some success, but is not generally applicable across all base oil and additive types. Current literature establishing a correlation of ASTM D943 results to PDSC results is not available. The ASTM D943 test is very critical for turbine oils, but its duration is typically over 2000 h, so there is a need for developing a rapid PDSC test which correlates well with the ASTM method. Common to all of the PDSC techniques highlighted above are varying degrees of precision problems, difficulty in measurement of oxidation stability and correlation to standard oxidation stability tests.

To resolve the problems associated with the PDSC method, a research program was directed toward optimizing those test parameters such as temperature and pressure of the calorimeter cell, heating rate, gas flow, sample size, and sample pan types in an effort toward improving test procedures to get more accurate and repeatable results. This paper describes the effect of these test variables on oxidation induction time (OIT) and its repeatability as well as the optimization of a new test procedure using a soluble metal catalyst and its correlation to the ASTM D943 oxidation stability test.

2. Experimental

2.1. Apparatus

The PDSC method was developed on a TA Instruments (New Castle, DE, USA) unit, which consists of a TA 2920 thermal analyzer, a 2920 CE PDSC cell, an oxygen cylinder, a flow meter and a computer for data recording and further processing.

2.2. Sample pans

Three types of aluminum sample pans (TA Instruments) were used for comparison in this study. One pan type is the flat bottom aluminum pan (TA “non-hermetic”) mostly used for solids. The second pan was a solid fat index (SFI) pan, which is ideal for wax, grease or oil samples. They contain a raised platform in the center of the pan where the sample sits and this prevents the sample from wicking up the sides of the pan. The third pan type is the hermetic pan mostly used for liquids. It can be used as an open pan or as a hermetically sealed pan with airtight seal that can resist higher internal pressures. Hermetic pans containing a top perforated with a pinhole are also available. In studying oxidation, open pans (sample pans without lids) or hermetically sealed pinhole pans are used most often. The approximate diameter of these pans is 6.7 mm.

2.3. Reagents and materials

Extra pure (99.6%) and dry oxygen, indium (99.9% pure), cupric naphthenate (in mineral spirits) containing 6% copper (Pfaltz and Bauer Inc.) were used in the present study. Mineral oil based industrial lubricants were used as supplied by Equilon LLC (Houston, TX) containing a commercial anti-oxidant additive package. They were denoted as AS-1 through AS-12. Table 1 presents some physico-chemical properties of the base oils used in making these lubricants as measured by standard ASTM test methods. The American Petroleum Institute (API) has developed a protocol for classifying base oils in terms of their chemical composition as shown in Table 2. The oxidation performance of lubricants AS-1 to AS-12 is outlined in Table 3. The fully formulated (FF) oils (AS-1 to AS-6) contain a commercial turbine oil additive package, which contains an aminic anti-oxidant, rust inhibitors, anti-foamants and demulsifiers. The oils AS-7 through AS-12 contain an aminic anti-oxidant alone (AO) with no other additives.

2.4. Calibration

The baseline and temperature calibration was done as per the TA Instruments operator manual at different pressure settings of oxygen maintaining flow

Table 1
Physico-chemical properties of base oils used in making finished lubricants

Samples	Sulfur (ppm) D5354	Nitrogen (ppm)	KV ^a at 100 °C (cSt)	KV ^a at 40 °C (cSt)	Viscosity index	API group
BO-1	3991	41	5.90	39.20	98.6	I
BO-2	8	0	5.48	33.12	101.7	II
BO-3	6	0	5.19	28.64	117.3	II
BO-4	13	0	6.01	38.72	109.4	II
BO-5	3	0	6.16	39.05	113.1	II
BO-6	7	0	5.97	32.85	129	III

^a Kinematic viscosity in centistokes (cSt).

at 400 ml/min. At elevated pressure, there was some change in the melting point of indium (157.4 °C under 3500 kPa of oxygen), which was used for the standard calibration temperature, from that found at ambient pressure (156.6 °C).

2.5. Sample preparation

For those samples where a soluble catalyst was used, different concentrations of cupric naphthenate (CuN) solution ranging from 1 to 2 µl/g of lubricant were used. The mixture was then kept airtight at ambient temperature overnight (18 h), so that the CuN diffused completely in the oil. The vial was then put on shaker for 1 min prior to analysis to have complete intermixing.

2.6. Test procedures

Two types of experiments can be carried out using the PDSC equipment. The first experiment maintains the temperature at a set value (isothermal) and determines the time required for the onset of a large increase in heat release (oxidation induction time). Alternatively, the sample can be heated at a programmed

rate (temperature ramp) and the temperature determined where large increases in heat occur (oxidation onset temperature). In this study, a great deal of attention was given to finding the conditions that yielded an optimum amount of reproducible information.

To perform the test, 2.0 µl of neat oil or prepared oil-catalyst solution was weighed into a new aluminum flat bottom sample pan and the sample was spread evenly on the flat surface. The uncovered pan containing the sample was placed on the front platform (sample platform) in the PDSC cell and an empty pan was placed as a reference on the rear platform. The cell was then capped and all the valves were closed with exception of outlet valve. The cylinder regulator was then adjusted to deliver the desired pressure. The inlet valve was slowly opened and oxygen was purged through the cell three times to displace the ambient air and finally, pressure was allowed to reach a constant

Table 2
API lubricant base stock categories

API group	Saturates (%)	Aromatics (%)	VI ^a	Sulfur ^b (%)
I	<90	>10	<120	>0.03
II	>90	<10	>80, <120	<0.03
III	>90	<10	>120	<0.03

^a Viscosity index by ASTM D2270.

^b Sulfur content by any of the following: ASTM D2622, D4294, D4927, D3120.

Table 3
Oxidation performance of lubricants

Lubricating oils	API group	Base oil	ASTM D943 (h)
Fully formulated (FF) lubricating oils			
AS-1	I	BO-1	2700
AS-2	II	BO-2	4100
AS-3	II	BO-3	5500
AS-4	II	BO-4	4100
AS-5	II	BO-5	5500
AS-6	III	BO-6	5400
Lubricating oils with anti-oxidants only (AO)			
AS-7	I	BO-1	850
AS-8	II	BO-2	1500
AS-9	II	BO-3	5300
AS-10	II	BO-4	3000
AS-11	II	BO-5	5500
AS-12	III	BO-6	5300

Sample: Lubricating oil
Size: 2.000 mg
Method: Oxidation induction method

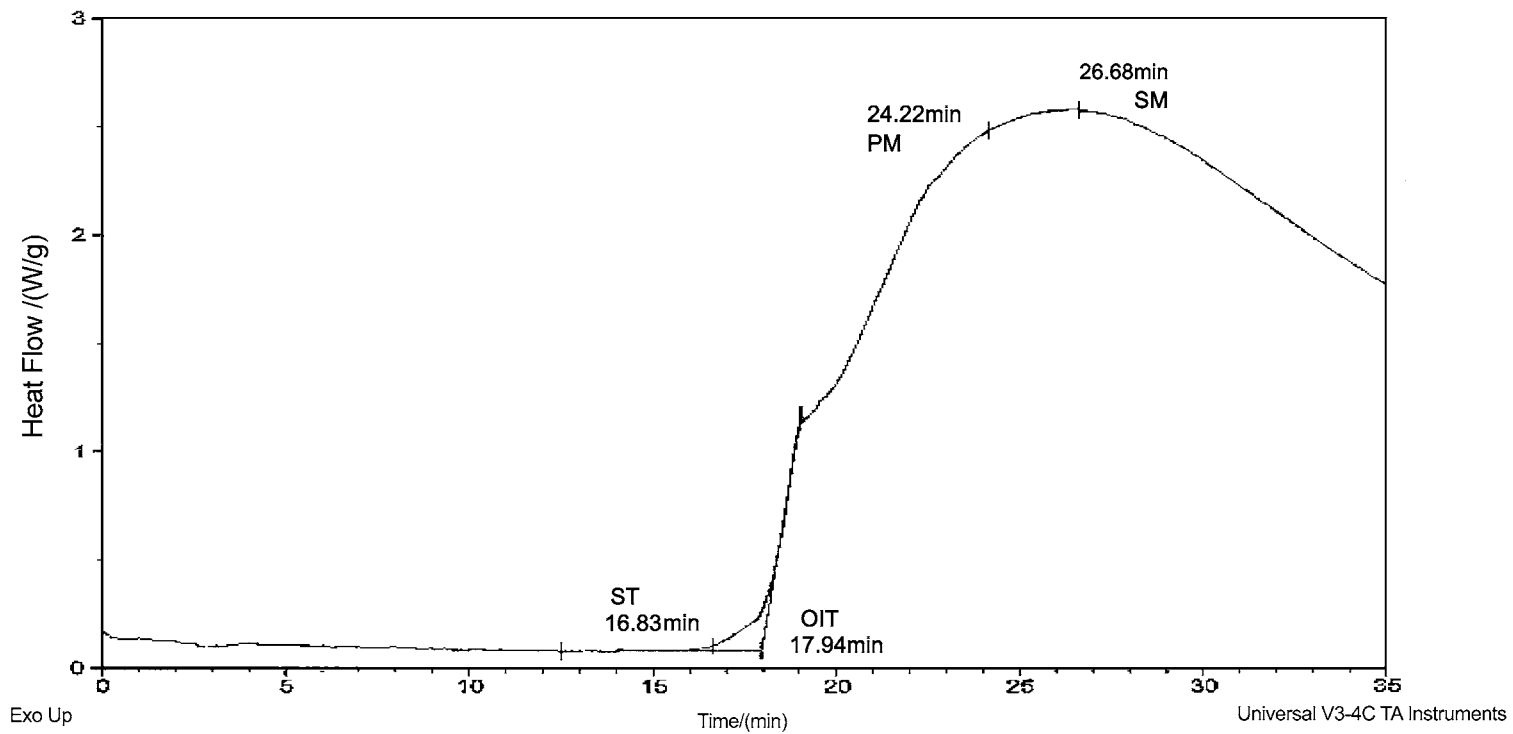


Fig. 1. Typical PDSC isothermal curve for lubricating oil.

level. In the constant pressure operational mode, the outlet valve was opened and adjusted to give a flow of 100 ml/min. For oxidation onset temperature measurements (temperature ramp) at various pressure settings, a 10 °C/min heating rate was used. In isothermal methods for measuring oxidation induction time (OIT), the sample temperature was programmed to increase at a rate of 40 °C/min from 30 °C to desired test temperature followed by equilibration at this temperature. Subsequently, an iso-track segment of sufficient length (10–120 min) was maintained to observe the thermal transition.

After the test was completed, the inlet valve on the cell was closed and the pressure was released by opening the pressure release valve. For the next test, the cell was then allowed to cool to 30 °C and cleaned using a tissue wetted with toluene. The cell was cleaned (by thermal desorption) after every three to four measurements to remove any accumulated organic matter to ensure safe operation. All other experiments with different conditions of temperature, pressure, flow rates, catalyst concentrations were then performed in a similar way.

2.7. Terminology

A sample isothermal curve of heat flow versus time for a fully formulated lubricant is shown in Fig. 1. The oxidation induction time (OIT), peak maximum (PM), signal maximum (SM), start time (ST) were determined from the thermogram. If more than one oxidation exotherm is observed, the oxidation induction time for the largest exotherm was reported. OIT is the time determined as the intersection of the extrapolated baseline and a line tangent to the oxidation isotherm constructed at its maximum rate. Peak maximum (PM) is the peak's point of maximum deviation from a linear baseline drawn between two points on a thermal curve. Signal maximum (SM) is the maximum signal value between two selected points on a thermal curve. Start time (ST) is the time of first deviation from the baseline, when primary oxidation products begin to form in the lubricating oil matrix. Oxidation temperature (OTemp), start temperature (STemp) and signal maximum (SM-Temp) in a temperature ramp method are the corresponding temperatures related to OIT, ST and SM, respectively, in an isothermal experiment.

2.8. ASTM D943 (TOST)

The turbine oil oxidation test (TOST) was used to evaluate the oxidation stability of lubricants as per the ASTM D943 method. In this procedure, a mixture of lubricant (300 ml) and water (60 ml), are exposed to oxygen at a rate of 3.0 l/h in the presence of solid metal iron-copper coil catalyst at 95 °C. The hours taken by the sample to reach a total acid number of 2.0 mg KOH/g is reported as the ASTM D943 value. Typical values range from 2000 to 10,000 h.

2.9. Statistical methods

A professional statistical software package, Minitab Release 12.0 (Minitab, State College, PA), was used in the current study. This package performs statistical analysis of the numerical data including linear regression. A “stepwise” multiple-regression was also performed using ASTM D943 values as the response variable and OIT, SM, ST and PM as predictor variables. Different regression equations with different predictor variables were compared for best fit, residuals and residual standard error (S), coefficient of determination (R^2) and R^2 adjusted for degrees of freedom [$R^2(\text{adj})$]. The selected model for predicting ASTM D943 values was based on highest $R^2(\text{adj})$, R^2 and lowest S . Some of the DSC parameters were evaluated using factorial designed experiments with the help of Minitab software.

3. Results and discussion

3.1. Onset temperature studies using the temperature ramp method

An onset temperature study was performed at 700 kPa oxygen, 150 ml/min flow rate with 2 μ l of sample in hermetically sealed pinhole aluminum pans. The temperature was ramped to 250 °C at various ramp rates of 1, 5, 10, 15 and 20 °C/min to measure start temperature (STemp), oxidation temperature (OTemp) and signal maximum for temperature ramp experiments (SM-Temp). The heat flow remained relatively constant until oxidation of the sample began, releasing energy. The main advantage of this test is that it can be applied to a wide variety of samples

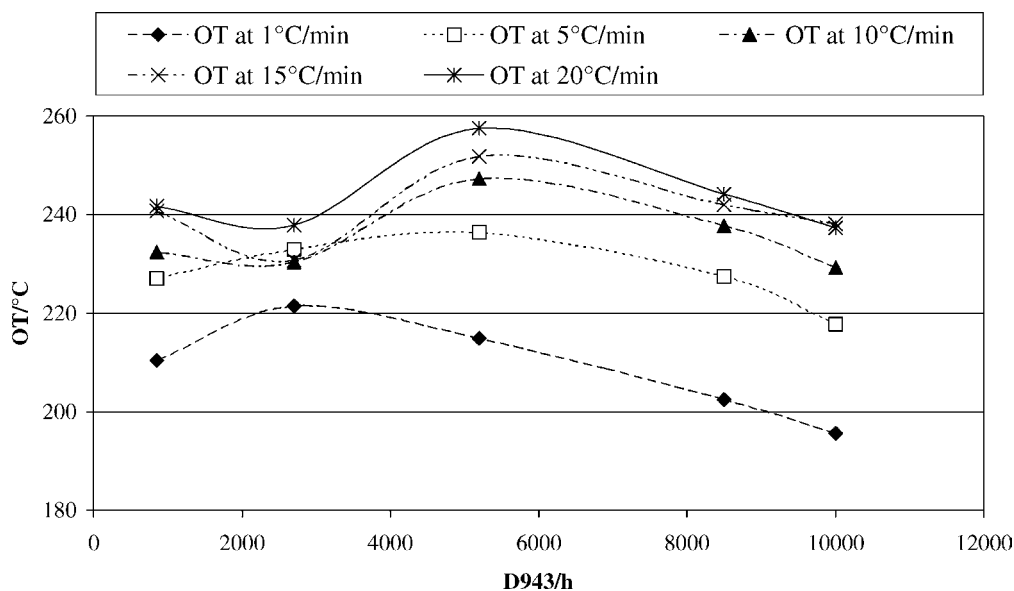


Fig. 2. Relationship between D943 data and onset temperatures at various ramp rates (700 kPa oxygen with flow rate of 150 ml/min, Al pinhole hermetic sample pans).

and it can be used for kinetic analysis. The parameter OTemp at different ramp rates were compared with ASTM D943 test results shown in Fig. 2. The OTemp first increased with ASTM D943 results, but then started decreasing, which was not expected. The kinetic analyses [28] of these experiments for different lubricants provide parameters like individual activation energy (E_a), specific rate constant (k) and half-life period ($t_{1/2}$). Due to the time-consuming nature of these experiments only five lubricants were tested. The E_a for five different lubricants varied in the range 40–140 kJ/mol, which resulted in a subsequent variation in k as well as $t_{1/2}$. On plotting these parameters versus ASTM D943 results, a similar trend to Fig. 2 was observed. It is apparent that neither the raw data (OTemp, STemp, SM-Temp), nor the kinetic data (E_a , k , $t_{1/2}$) provided useful correlations with D943 results for the temperature ramp method.

In a previous study, it has been shown that use of a soluble catalyst improved correlations with engine tests [33]. To evaluate the activity of catalysts, all samples (AS-1 to AS-12) were prepared with 1.2 μ l of CuN solution in 1 g of lubricating oil and testing was done according to temperature ramp method reported by Fox et al. [29] with some modifications.

The temperature programming was kept the same, but sealed capsules were replaced by hermetically-sealed aluminum sample pans with an oxygen pressure of 2200 kPa. The temperature was ramped at 10 °C/min to 150 °C to rapidly approach the onset temperature, and after this, the heating rate was reduced to 3 °C/min up to 300 °C. The reduced heating rate provided accurate results and, when combined with the initial rapid rate, the test was completed in a reasonable time. These test conditions were then used to test neat lubricants as well as lubricant solutions with catalyst. STemp, OTemp and SM-Temp were obtained from these test conditions for various samples and these parameters were compared for possible correlation with ASTM D943 test results. Table 4 shows the regression constant (R^2) values between STemp and D943 results. Of the three variables, STemp was found to give higher

Table 4
Regression model results for neat oils and catalyzed oils

	STemp-neat oils	STemp-oils with catalyst
R^2 (FF)	0.69	0.67
R^2 (AO)	0.29	0.74
R^2 (FF + AO)	0.4	0.55

R^2 values compared to OTemp and SM-Temp. In the case of oils with catalyst, the R^2 value is reasonably high for samples having the same additive package (fully-formulated (FF) or anti-oxidants only (AO)), but is lower when the samples are combined into a single group including both additive packages (FF + AO). Another noticeable difference is between neat lubricants and lubricants with catalyst. In general, the R^2 value improves for samples with soluble catalyst, but the value is still not sufficiently high for predicting D943 values accurately. Initial results also indicated that it is difficult to obtain sufficient sensitivity to distinguish between various samples with onset temperature measurements using the temperature ramp method.

3.2. Oxidation induction time studies using isothermal method

OIT measurements using the isothermal method have a better chance to provide analysis sensitivity by providing sufficient difference in the OIT of oils with similar ASTM D943 values. However, the results cannot be used for kinetic analysis, although as mentioned above, the kinetic parameters did not provide a good correlation with ASTM D943 values for the temperature ramp experiments. Due to immeasurably short induction times, quantitative measurements for base oils containing no additive, cannot be made using this method. As a starting point, the conditions described in the ASTM D6186-98 PDSC method (oxygen pressure 2921 kPa, open aluminum hermetic pans, isothermal temperature 195 °C) were used initially to evaluate some of the finished lubricants, but the results obtained from these test conditions did not correlate well with ASTM D943 test results. Specifically, the observed OIT decreased with increasing D943 values. Therefore, an extensive study was made to optimize the experimental protocol for an isothermal method by adjusting variables such as temperature, pressure, flow rate, sample size, start temperature to improve the repeatability and accuracy of the results, and to generate DSC parameters (OIT, ST, SM), which can provide good correlation with ASTM D943 results. Use of a soluble metal catalyst has already shown improvement, so all the optimization work was done using metal catalysts. It has been shown that copper naphthenate behaves

as pro-oxidant (catalyst) at lower concentrations, and a strong anti-oxidant (oxidation inhibitor) at higher concentrations [11]. Therefore, the concentration of catalyst also needed to be optimized so that the catalyst would accelerate oxidation in our experiments.

3.2.1. Isothermal method: effect of experimental variables on repeatability of OIT

Due to the great number of experimental variables and sample compositions available for testing, repeatability is an important problem in DSC methods. We also experienced repeatability problems with some oils such as AS-1 which exhibited a coefficient of variation (CV) of 20%, while AS-3, AS-4 and AS-11 showed a CV of 8.0%. As a result, these oils were used to study PDSC repeatability. Previous studies [21,25] have attributed repeatability problems to surface topography and the metallurgy of pans, both of which are out-of-control factors. They also found that DSC pan impurities had an effect on the variability of OIT. They traced iron and chromium impurities in the aluminum pans using energy dispersive X-ray (EDX) analysis. Iron impurities caused a decrease in oxidation stability, while increasing amounts of chromium stabilized the oxidation process [21]. They also concluded that flat aluminum pans displayed the lowest standard deviation and ascribed it to the surface of the pans, which is very flat, clean, homogeneously corrugated with no visual defects and contamination, compared to SFI and hermetic pans. The high standard deviation with SFI pans was attributed to iron contaminants through EDX. For hermetic pans, deviation was attributed to blemishes present on the surface as studied by scanning electron microscopy [25].

To determine the effect of different variables on repeatability, multiple runs were done at different conditions by varying one parameter at a time. It was found that pressure (500, 1000, 1500, 2200, 3000 kPa) makes a significant contribution to repeatability. Higher pressures in the DSC cell yield lower standard deviations on average in OIT, while lower heating rate (40 °C/min) leads to slightly lower data variation as compared to higher heating rate (100 °C/min). The effect of sample mass (0.5, 1.0, 2.0, 3.0 mg) on OIT is lowest at high sample masses. With 3.0 mg of sample, the OIT value changes 1.5 min (ca. 6%) for each 0.5 mg change in sample mass, while with 0.5 mg

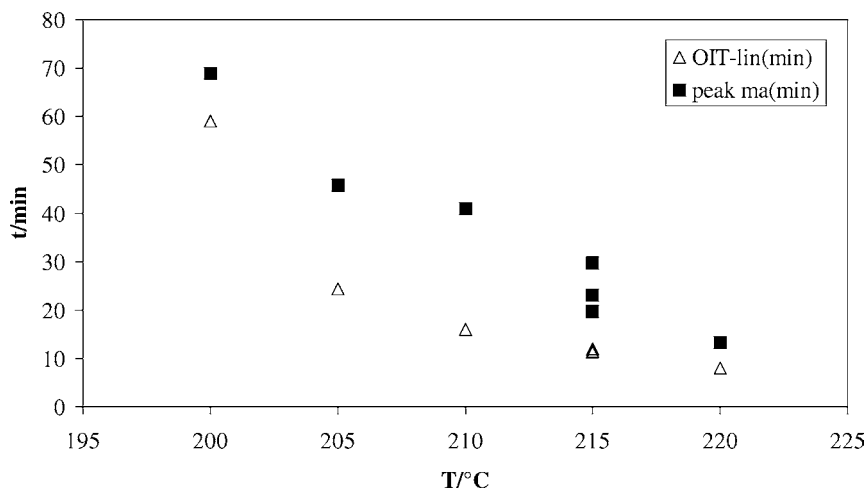


Fig. 3. Variation in PM and OIT with temperature (lubricating oils, hermetically sealed pinhole Al sample pan, 3000 kPa oxygen pressure in constant pressure mode with flow rate 100 ml/min, heating rate 10 °C/min, isothermal at test temperature).

of sample, OIT changes 2.1 min (ca. 12%) for each 0.5 mg change in sample mass. It logically follows that with low sample mass, there are chances of large variation in the OIT with a small change in sample mass, while this risk is lower for higher sample mass. On average, higher gas flow rates up to 400 ml/min yield lower values of standard deviations in OIT than do the lower flow rates (100, 250 ml/min) or the no flow condition. At higher flow rates of oxygen, hermetic pinhole pans give slightly lesser data variation than SFI pans followed by hermetic open and flat bottom (non-hermetic) sample pans. Hermetic open pans give lesser data variation at lower flow rates of oxygen than hermetic pinhole pans. The peaks are sharp in open pans and broad in sealed hermetic pans. The possible reason for this may be that a larger surface area of oil is in direct contact with oxygen, so a faster rate of heat release occurs for open pans compared to sealed hermetic pans with pinholes, where the rate of heat release is slow, thus giving broader peaks.

3.2.2. Isothermal method: effect of experimental variables on OIT

This study has been concerned with defining proper operating conditions and demonstrating the responsiveness and sensitivity of the technique. The dependent variables for developing an oxidation method

include: temperature, pressure, heating rate, sample mass, gas flow rate, catalyst concentration, sample pan types. The discussion will be in two parts: (1) the effect of variables for uncatalyzed neat oils and (2) the effect of variables in presence of catalyst in oil samples. Fig. 3 illustrates the effect of temperature on OIT and PM. As the temperature increases, OIT decreases exponentially, while PM decreases more linearly. Fig. 4 shows the dependence of OIT on oxygen pressure in the case of hermetically-sealed aluminum pinhole pans. The OIT changed from 33 to 12 min when the pressure was changed from 700 to 3000 kPa under an oxygen atmosphere, so working at high-pressure will considerably reduce the experimental time also. At 125 kPa (resembling atmospheric pressure; data not shown) the OIT is 60 min. The temperature dependence of OIT is mainly associated with kinetic effects (reaction rate increases with temperature). Increasing oxygen pressure increases the local oxygen concentration as well as the diffusion rate of oxygen as the number of moles of oxygen per unit volume increases. As a result, OIT determined in a pure oxygen environment is usually lower than that obtained in air provided other experimental conditions remain the same. On the basis of the above observations the PDSC optimum test conditions described in Table 5 were used for generating OIT data on uncatalyzed finished lubricants.

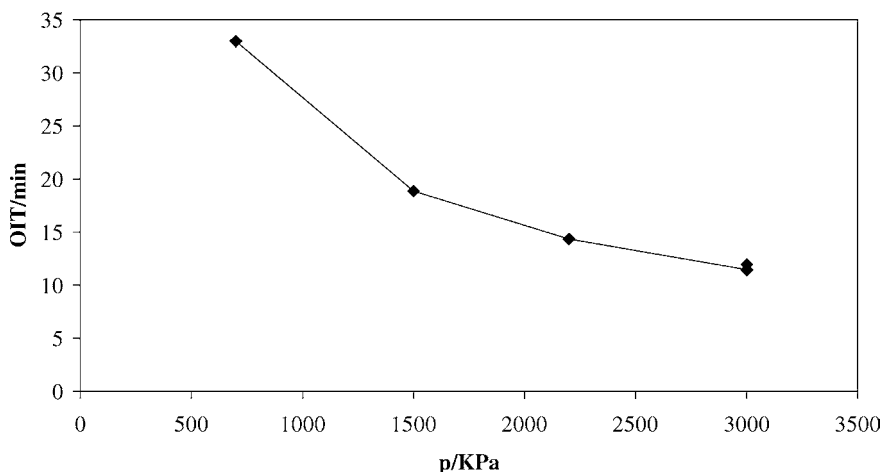


Fig. 4. Variation in OIT with pressure (lubricating oils, hermetically sealed pinhole Al sample pan, oxygen in constant pressure mode with flow rate 100 ml/min, heating rate 10 °C/min, isothermal at 215 °C).

Using the FF group of uncatalyzed oils detailed in Table 3, a good correlation ($R^2 = 0.87$) with D943 test results is observed. Unfortunately, however, the correlation fails badly ($R^2 = 0.023$) in case of the AO group of oils. And on combining the two groups (FF and AO) the R^2 does not exceed 0.127. The possible reason for this failure is that PDSC test conditions do not exactly reflect the actual ASTM D943 test conditions that include a solid metal catalyst and water. Therefore, it was decided to pursue further studies with the use of a catalyst in the PDSC method.

Two oils, AS-3 and AS-8, both containing API group II base oils with D943 values of 5500 and 1500 h, respectively, representing an upper and lower limit, were used to establish an experimentally designed relationship between experimental variables and OIT. A factorial designed experiment 2^5 was used

to evaluate the following DSC parameters: temperature (150–170 °C), pressure (500–3000 kPa), sample pan type (hermetic open and hermetic pinhole), catalyst (CuN in mineral spirits, 6% copper) concentration (1–10 μ l) for the oils AS-3 (a FF oil) and AS-8 (a AO oil). Other parameters evaluated were gas flow rate, heating rate and sample mass. Fig. 5 shows the influence of variables and their various combinations on OIT. Although the influence of 30 variables and their combinations on OIT was shown, it was observed that temperature has the most pronounced effect on OIT, followed by catalyst concentration and pressure (Fig. 5). The main effect plot in Fig. 6 illustrates the results of this experiment. Increasing the temperature by 20 °C will change the OIT drastically. Altering the catalyst concentration from 1 to 10 μ l and varying pressure within the cell also changes the OIT greatly.

Table 5
PDSC conditions for uncatalyzed and metal catalyzed experiments

	Uncatalyzed experiment	Metal catalyzed experiment
Catalyst concentration	No catalyst	1 μ l in 1 g of lubricating oil
Pan type	Al hermetic open/flat bottom (non-hermetic) pans	Al flat bottom (non-hermetic) pans
Temperature	170 °C	165 °C
Pressure	2920 kPa (425 psig) oxygen	500 kPa oxygen
Sample size	2.0 mg	2.0 mg
Gas flow rate	400 ml/min	400 ml/min
Heating	30–170 °C at 40 °C/min	30–165 °C at 40 °C/min

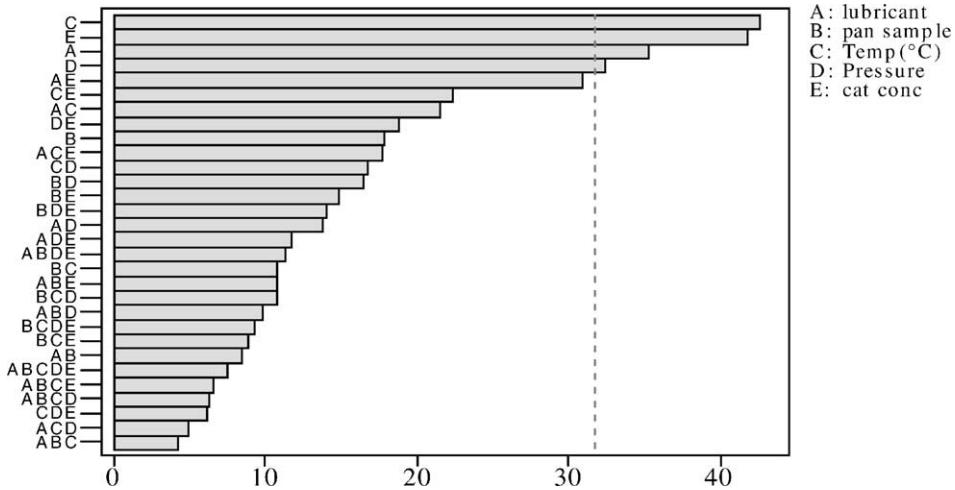


Fig. 5. Pareto chart of parameter effects on OIT.

The average OIT changed from 48 to 17 min when the pressure was changed from 500 to 3000 kPa under an oxygen atmosphere. Similarly the average OIT changed from 52 to 11 min when catalyst concentration was changed from 1 to 10 $\mu\text{l/g}$ of oil. Fig. 7 shows the interaction of one parameter with another and their combined effect on OIT can be studied. For example, the effect of the pans is the same in both oils and, similarly, pressure has almost the same effect. For temperature and catalyst, however, the decrease in OIT is much more significant in oil AS-8 as compared to AS-3. At low temperatures and lower catalyst concentration, there is a larger difference in OIT, but at higher temperatures and high catalyst

concentration, the difference decreases substantially. Similarly, we can look at the interaction of pan types, temperature, pressure and catalyst concentration with other parameters. The effect of catalyst concentration on OIT was also studied for two additional lubricants: AS-5 (FF) and AS-11 (AO). As shown in Fig. 8, lower concentrations of CuN (up to 7 $\mu\text{l/g}$) act as a catalyst. After reaching a minimum at 7 $\mu\text{l/g}$, the OIT increases again, thereby acting as anti-oxidant in this concentration range. This observation is in accordance with a previous report [11]. Other factors such as sample pan type, gas flow rate, heating rate and sample mass contribute less significantly to changes in OIT.

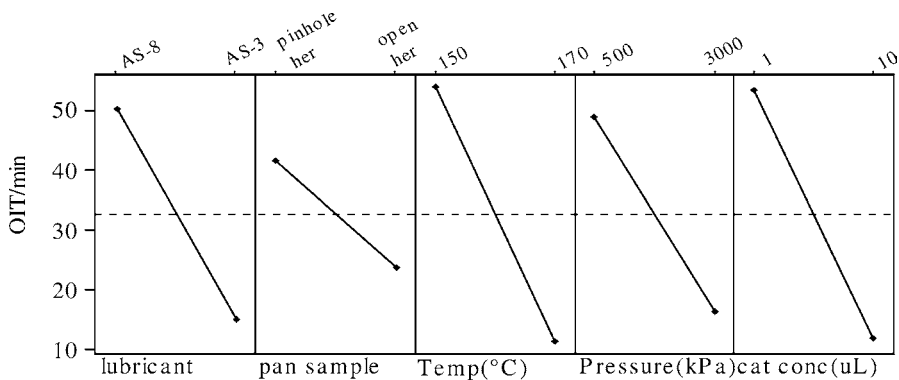


Fig. 6. Main effects plot for OIT.

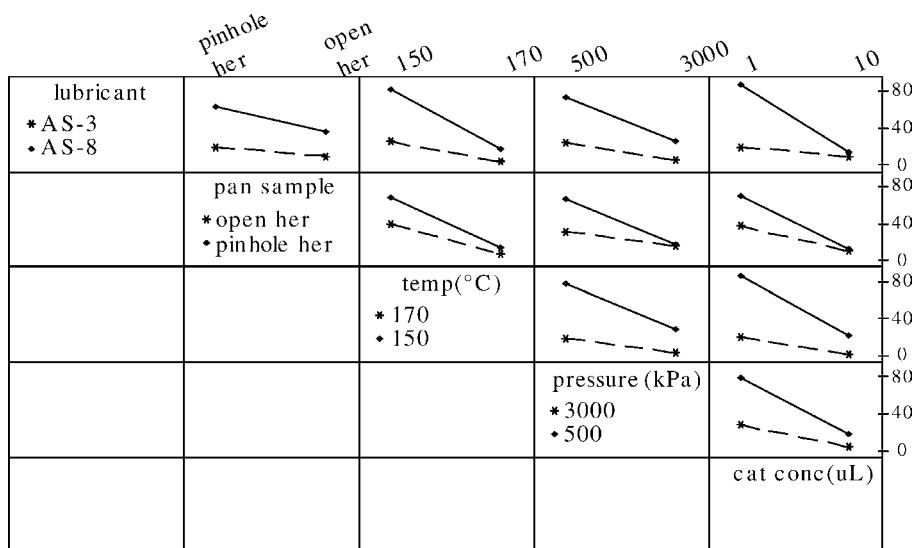


Fig. 7. Interaction plot for OIT.

3.2.3. Isothermal method: optimization of experimental variables

On the basis of the above results, the experimental conditions described in Table 5 were established for the soluble metal catalyzed oxidation experiment. To determine a repeatability value for the isothermal method, data were generated for sample AS-12 on different dates. In all cases, the observed values were reasonably close to the average value as shown in Table 6.

The coefficient of variation, determined as the percentage standard deviation of the average value, is well within the acceptable limit for the PDSC instrument.

As shown in Fig. 9, this method was used to generate PDSC oxidation data on 12 catalyzed lubricating oils. For both groups of lubricants (FF and AO), OIT predicts the ASTM D943 results very well, as the R^2 for both these groups are 0.76 and 0.89, respectively, although some scatter is evident at higher ASTM D943

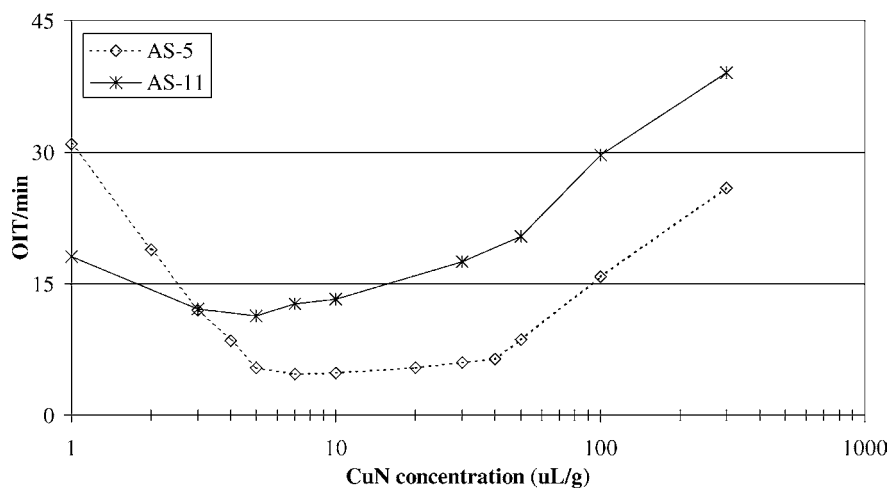


Fig. 8. Effect of catalyst concentration on OIT.

Table 6
High-pressure oxidation repeatability data on oil AS-12 using a soluble metal catalyst

Date	Oxidation induction time (min)	Peak maximum (min)	Signal maximum (min)	Start time (min)
10 May 2001	16.5	20.4	20.6	15.5
10 May 2001	15.0	19.0	19.1	14.2
10 May 2001	15.8	19.8	20.0	15.1
14 May 2001	16.4	20.4	20.6	15.5
14 May 2001	17.2	21.3	21.5	16.8
14 May 2001	17.7	21.8	21.9	16.9
14 May 2001	15.5	19.3	19.5	14.9
15 May 2001	16.5	20.1	20.5	16.0
15 May 2001	17.1	21.2	21.3	16.9
Average values	16.4	20.4	20.6	15.8
Standard deviation	0.9	0.9	0.9	1.0
Coefficient of variation	5.3	4.6	4.5	6.1

values. If the two groups are combined together, the predictability is again poor ($R^2 = 0.30$) if only OIT is used as predictor. Since the two groups contain different additives, it is likely that two different oxidation paths are being followed by the two groups. The group containing only anti-oxidants only shows lower values of OIT than the one containing the fully formulated lubricating oils, which contain anti-oxidants plus rust inhibitors, anti-foamants and demulsifiers. Under the present experimental conditions, the presence of other additive components appears to delay the oxidation. If two variables, ST and SM were used in establishing correlation to D943, the R^2 value increased to 0.69

from 0.30. On adding another variable, OIT, to these two variables, the R^2 value increased to 0.85. Upon using all the four variables (OIT, ST, SM and PM) the R^2 value increases to 0.93. This model was also tested for cross-validation which provides an estimate of true predictive power of the developed model by checking the reliability of the predicted values for unknown samples. For cross-validation of the regression, data for 10 samples (out of 12 samples) is used to develop a regression to predict the ASTM D943 values of the remaining two samples that are not used in the regression. This is repeated for each pair of samples and the reported cross-validation coefficient $R^2(CV)$

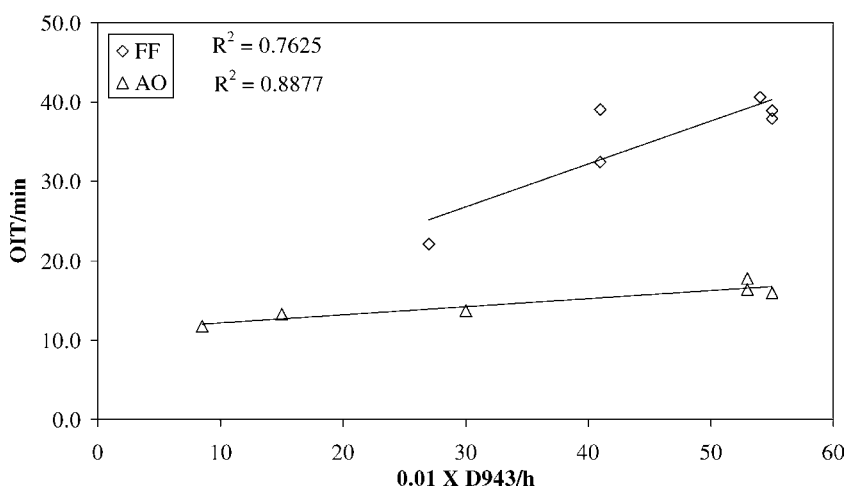


Fig. 9. Correlation of D943 values with OIT for fully formulated (FF) and anti-oxidant only (AO) lubricating oils generated using catalyst. Experimental conditions as defined in Table 5.

Table 7
Statistics of cross-validation

Variable	N	Mean	Minimum	Maximum
R^2 (CV)	6	93.88 (93.3)	87.8	97.6
R^2 -adj(CV)	6	88.98 (89.5)	78	95.7
S(CV)	6	509.9 (543.4)	369	639.8
Residual(CV)	12	−196	−1566	1174

is the average of all six. It was found that the R^2 (CV) value for the average of six R^2 values generated in cross-validation experiments (Table 7) is the same as the R^2 for this model.

In developing correlations, if a true relationship is present between two variables, the whole set of samples as well as its various subsets should have almost same correlation constant (R^2). Using the above conditions (Table 5), although the subsets (AO and FF) have higher R^2 values, the whole set has very low R^2 value, so there is a strong possibility that OIT does not reflect a true relationship with D943 results for the combined FF and AO group of oils. In view of this, further optimization in pressure, temperature, catalyst concentration and sample pan type led to the PDSC conditions described in Table 8.

Higher cell pressure (2200 kPa) gave sufficient resolution in OIT values for different oils. Increased catalyst concentration to 1.2 $\mu\text{l/g}$, increased the R^2 value for the whole set. Since temperatures of 165 or 170 $^\circ\text{C}$ gave almost same R^2 values, an intermediate temperature (168 $^\circ\text{C}$) was also tried, which provided better resolution in OIT values. These revised PDSC conditions were then used for generating additional data on all oils.

Table 8
PDSC method comparison with ASTM standard method

	ASTM D6186-98	Current method
Catalyst	No	1.2 μl in 1 g of lubricating oil
Oxygen pressure (kPa)	3500	2200
Flow rate (ml/min)	100	400
Isothermal temperatures ($^\circ\text{C}$)	155, 180 or 210	168
Ramp rate ($^\circ\text{C}/\text{min}$)	100	40
Sample pans	Open SFI	Hermetic sealed pinhole Al pans
Sample size (mg)	3.0	1.0

3.3. Results of new PDSC isothermal test method

The OIT, SM and ST data generated on two groups of lubricants fully formulated (FF; AS-1 to AS-6) and anti-oxidants only (AO; AS-7 to AS-12) are summarized in Table 9 along with their ASTM D943 data. All the data points are an average of two to three test runs. The OIT values varied from as low as 7.0 min to well over 22.0 min in case of FF oils and 8.0–18.0 min in AO oils which is a desirable experimental range.

3.3.1. Influence of base oil on oxidation properties

Fig. 10 shows D943 values and OIT values for two groups of oils (FF and AO only). The plot is constructed so that in each pair, FF and AO, the base oil was the same. There are significant differences in D943 values for base oils BO-1, BO-2 and BO-4 having two different additives, while the base oils BO-3, BO-5 and BO-6 show small differences even on using two different additives. On the other hand, the OIT values for almost all the base oils show no difference on using two different additives. These results show that the API group of the base oil is also important in determining the oxidation stability. PDSC oxidation of API group I oil (BO-1) and low viscosity index (VI) API group II oils (BO-2 and BO-4) apparently do not follow the same oxidation mechanism in ASTM D943. While higher VI API group II oils (BO-3 and BO-5) and an API group III oil (BO-6) follow the same trend in oxidation using the PDSC and ASTM D943 methods. It may be inferred that additive type has more impact than base oil type on the oxidation stability of API group I and low VI group II lubricants, while in higher VI groups II and III oils, base oil itself is a more dominant factor than the additive type.

3.3.2. Correlation of ASTM D943 values with results of new PDSC isothermal method

The relationship observed between ASTM D943 results and OIT, ST and SM for the FF and AO groups is shown in Figs. 11 and 12, respectively. ST ($R^2 = 0.80$) as well as OIT ($R^2 = 0.79$) for FF group of oils predict D943 values better than the signal maximum ($R^2 = 0.74$). In the case of the AO group, OIT ($R^2 = 0.74$) provides a better predictability than ST ($R^2 = 0.68$) and SM ($R^2 = 0.67$). In both groups, scatter increases at higher D943 values. Fig. 13 shows the relationship of DSC data with D943 values on

Table 9
High-pressure oxidation data on lubricating oils using the catalyst

Lubricating oil samples	ASTM D943 (h)	Oxidation induction time (min)	Signal maximum (min)	Start time (min)
Fully formulated (FF) lubricating oils				
AS-1	2700	7.6	9.6	6.5
AS-2	4100	13.3	21.3	13.1
AS-3	5500	17.9	27.4	17.1
AS-4	4100	14.0	25.6	13.6
AS-5	5500	16.4	26.0	16.2
AS-6	5400	22.9	36.8	22.6
Lubricating oils with anti-oxidants only (AO)				
AS-7	850	8.3	10.8	5.7
AS-8	1500	12.4	20.3	12.0
AS-9	5300	15.2	24.9	14.6
AS-10	3000	12.1	25.0	11.6
AS-11	5500	14.2	24.5	13.5
AS-12	5300	18.2	30.7	18.0

combining the two lubricant groups together. The OIT values for AO group was comparatively lower than the FF group of oils in the previous experimental conditions (Table 5, Fig. 9), but under the present test conditions, the OIT values for one group is comparable to the other group. In this case OIT ($R^2 = 0.61$) and ST ($R^2 = 0.63$) predicted the D943 value better than SM ($R^2 = 0.57$). The slopes of fitted lines of OIT, ST and SM are different and this means that OIT, ST and SM vary independently with D943 values, so these three together can be used as predictor variables for

multi-linear regression models for predicting ASTM D943 values more accurately.

If two variables are used in constructing a regression model, OIT and ST, the R^2 value increases from 0.61 to 0.64. On addition of another important variable to these two parameters, the API group base oil group used in the lubricant formulation (parameterized as 1, 2 and 3, for groups I, II, III, respectively), R^2 was observed to further increase to 0.70. Incorporation of more variables increased the R^2 value very little. If a variable is added to an equation, R^2 will get larger even

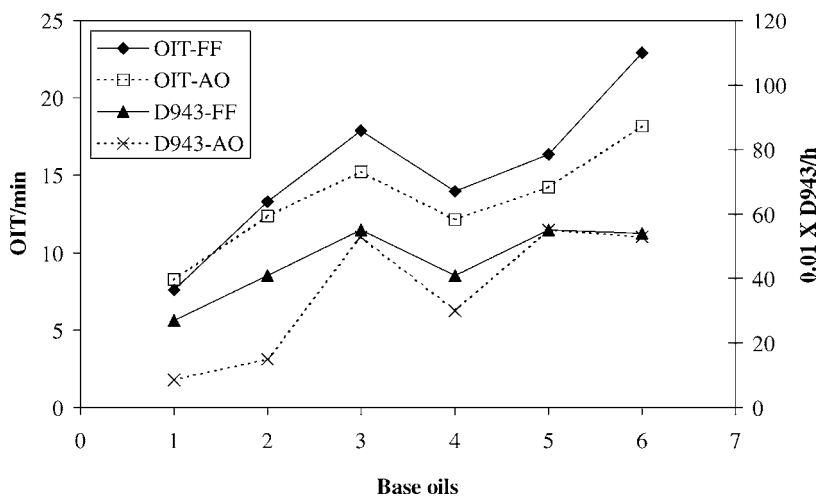


Fig. 10. Base oils with two sets of additives.

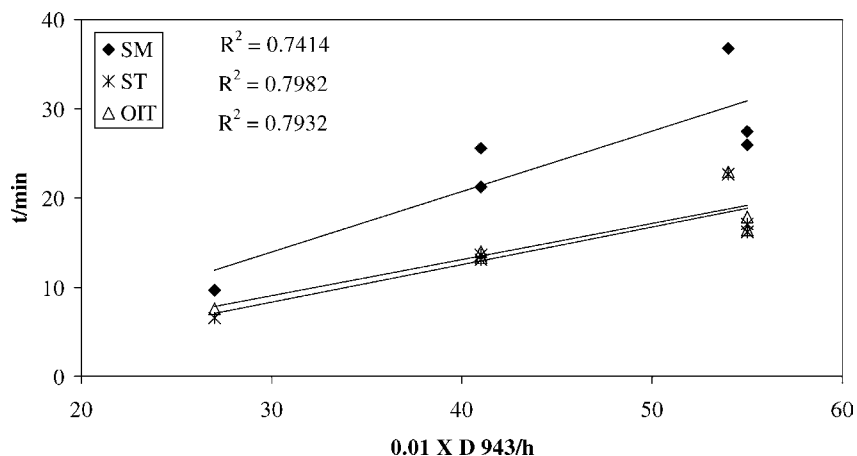


Fig. 11. Correlation of D943 values with OIT, ST and SM for FF oils. Experimental conditions as defined in Table 8.

if the added variable is of no real value. To compensate for this, Minitab statistical software provides another parameter $R^2(\text{adj})$, which is R^2 adjusted for degrees of freedom. The model using three variables exhibits an $R^2(\text{adj})$ value of 0.59, while for equation using OIT only it is 0.57. The estimated standard deviation about the regression line also decreased slightly on using three variables instead of one.

A coefficient of variation (cov) on the order of 20% for test-to-test repeatability is common in ASTM D943 test method, while the cov for lab-to-lab reproducibility can go as high as 33%. As a result, the

estimated standard deviation (10.7) for the model developed using PDSC parameters is acceptable in comparison to that of the ASTM D943 test method. In view of poor repeatability and reproducibility of ASTM D943 method itself, the correlation developed using PDSC data with R^2 value of 0.70 may be considered to be a successful attempt to predict ASTM D943 results.

The current PDSC method is compared to the standard ASTM D6186-98 method in Table 8. The current method uses a catalyst, which has two main advantages. The analysis time has been reduced considerably from 120 to 50 min. In the ASTM method, if OIT

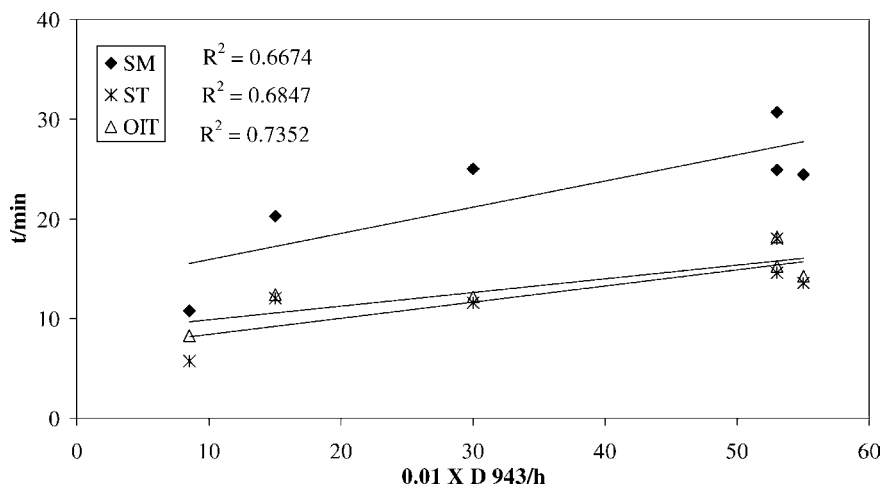


Fig. 12. Correlation of D943 values with OIT, ST and SM for AO oils. Experimental conditions as defined in Table 8.

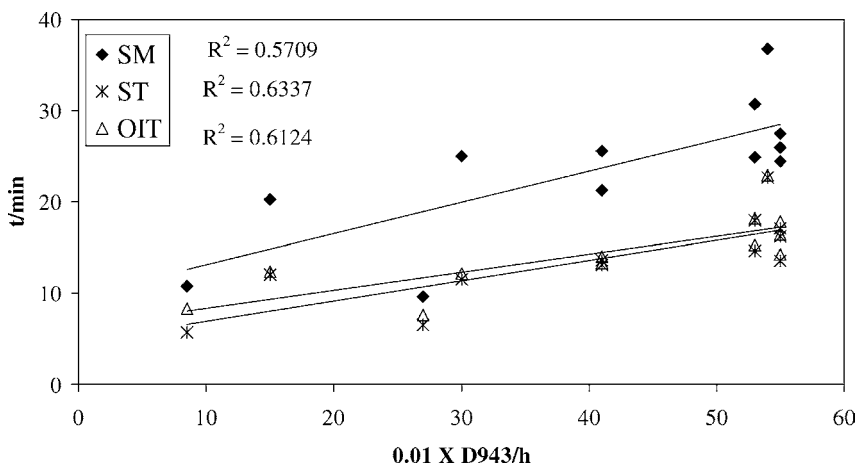


Fig. 13. Correlation of D943 values with OIT, ST and SM for all 12 (FF + AO) oils. Experimental conditions as defined in Table 8.

does not appear within a 10–120 min window, then the next higher or lower isothermal temperature has to be tried, so there is a possibility that for different oils, different isothermal temperatures are used. Unfortunately, under these circumstances, it will be very difficult to compare different oils for their oxidation stability. However, in current method all the samples can be tested at same temperatures. As the temperature is fixed in the current method, oils can be compared easily for their oxidation stability, simply by looking at their oxidation induction times. Another factor of comparison is repeatability. The coefficient of variation is less than 5% in the current method, while it is 20% or greater in ASTM method.

4. Conclusions

A new PDSC method has been optimized for industrial lubricating oils to generate important information on oxidation stability. The method developed is simple, fast and reliable with very little reliance on the skill of operator and has proved to be an effective method for screening of oxidation stability of lubricant formulations having the same additive package. The PDSC method using a soluble metal catalyst showed better results than the procedure using only neat lubricating oils. An attempt was also made to establish correlations with the ASTM D943 method. It was found that for a set of oils with the

same type of additive package, PDSC parameters showed good correlation with D943 data (R^2 value approaches 0.8). As a general trend, OIT, ST and SM increase with D943 values for formulations having the same additive package. On combining two sets of oils having different additive packages, ASTM D943 values can still be predicted, but with less accuracy. Further studies could also utilize PDSC to predict the oxidation performance of engine oils in the Sequence III high temperature oxidation test.

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