

## Oxidation Stability of PAO Oils Determined by Differential Scanning Calorimetry

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**Abstract**—The suitability of a pressure differential scanning calorimetry (PDSC) in monitoring the quality of synthetic base fluids has been investigated using polyalphaolefin (PAO) oils as an example. Induction period measured at 170, 180 and 190°C, and 3.53 MPa oxygen pressure was applied to characterize their oxidation stability. The PDSC method has proven to be simple and repeatable and requires only small sample size for testing. More importantly, it can be applied in differentiating the oxidation performance quality of PAO oils and is versatile enough for use in studying kinetic aspects of PAO oil oxidation which include the effect of temperature and antioxidant concentration. Additionally, the method appears to correlate well with a rotary bomb oxidation test (RBOT).

### 1. Introduction

High temperature oxidation stability of PAO oils varies significantly dependent upon the severity and effectiveness of hydrogenation in their manufacture. Also, the formation of peroxides during transport, storage and handling has a marked influence. In view of these, PAO manufacturers have long been seeking a simple test which lends itself to quality monitoring of PAO batches after manufacture, on delivery to blending plant and during long-term storage.

The use of PDSC to characterize the oxidation stability of lubricants has been investigated by many researchers, initially by Noel [1] in 1971, by Walker and Tsang [2] to examine ASTM III-C engine oils, by Hsu et.al [3] to correlate PDSC results with III-D engine oil performance and more recently by Zeman [4] to study thermo-oxidation of polyol ester-based aviation oils. Numerous claims have been made ranging from the simplicity of PDSC as a bench test to success in predicting the oxidation performance of lubricants in engines and mechanistic study of esters with varying chemical structure.

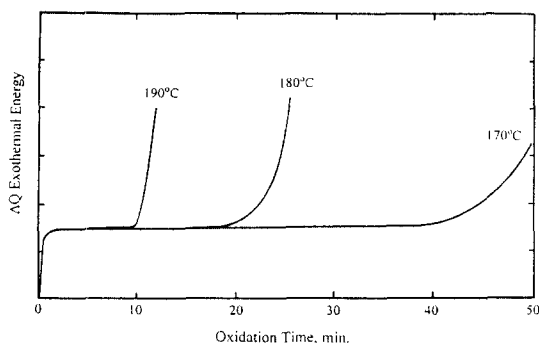
In view of these, our motivation behind this study was to investigate if PDSC is flexible enough to be used in differentiating batch-to-batch variations in the quality of PAO base oils and in studying kinetic aspects of PAO oxidation.

### 2. Experimental

All of the experiments were performed with a Du Pont Model 1090B Thermal Analyzer equipped with a Model 990 DSC module operating with a pressure DSC cell. Test conditions used were oxygen pressure, 3.5 MPa; temperature, 170, 180 and 190°C; catalyst, none and pan, aluminum open cup.

Each test run consists of a pre-determined isothermal oxidation of a PAO oil sample in the PDSC unit by applying the following procedure: Weigh  $6.0 \pm 0.1$  mg of test oil in an aluminum pan. Place the pan onto the sample platform in the cell, along with an empty pan of the same configuration on the reference platform. Close the cell and purge the cell of oxygen by pressurizing to 3 MPa with oxygen. Repeat the purge cycle three times. Slowly pressurize the cell to 3.5 MPa.

To bring the specimen the desired test temperature, set the cell heating rate to 160°C/min to 140°C, then at 80°C/min, the program mode to isothermal, and then start the test. Continue the scan drawing a thermogram by plotting thermal energy differential between oil sample and reference pan versus time until an oxidation exotherm is observed, thus resulting in a sharp break in the thermogram. Time to reach this break (inflection) point is defined as Induction Period (IP). Run triplicate tests and report the average value of triplicate determinations.



**Fig. 1. Typical DSC Thermograms of PAO-1 at Different Temperatures.**

**Table 1. Typical Physical Properties of PAO Base Stocks**

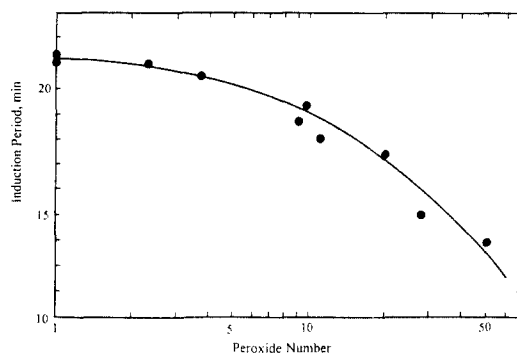
	PAO-1	PAO-2	PAO-3
Density, 15°C, g/cm <sup>3</sup>	0.827	0.853	0.860
Flash Point, °C	235	271	280
Pour Point, °C	-60	-43	-32
Viscosity, cSt			
40°C	27.2	405.0	1250
100°C	5.47	40.8	100.0
VI	139	150	168
TAN, mgKOH/g	<0.01	<0.01	<0.01

The total time required to heat the oil sample from room temperature to the test temperature was less than 1.5 minutes. For simplicity, this constant time was neglected in computing the IP.

A set of typical DSC thermograms of PAO-1 (Sample C) at different temperatures is shown in Fig. 1. Typical properties of laboratory prepared PAO base oils are summarized in Table 1.

### 3. Results and Discussion

Prior to a series of testings, the applicability of the PDSC method for IP determination was initially investigated by testing un-inhibited PAO fluids. Their oxidation at 180 and 190°C took place almost immediately. Even at lower temperatures, their IP values were relatively short and difficult to accurately define. However, PAO-1 containing an antioxidant, [4,4'-methylenebis(2,6-di-tert-butylphenol)], maintained an isotherm over 40 minutes at 170°C and at least 10 minutes at 190°C. Accordingly, the bisphenol at a concentration level of 0.25% by weight was used throughout this study unless oth-



**Fig. 2. Induction Period of PAO-2 as a Function of Peroxide Numbers (DSC Temperature=180°C).**

erwise specified.

In order to determine repeatability, ten IP measurements were made on an inhibited PAO-1 at 170°C. A mean IP value of 41.5 minutes was obtained with standard deviation of less than  $\pm 3.0\%$ .

#### 3-1. Effect of Peroxide Number

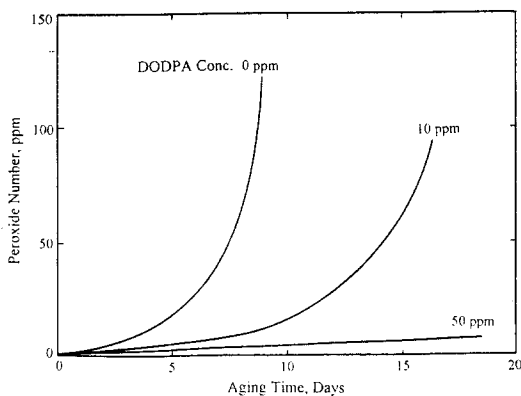
Hydroperoxide is a precursor for oxidation. Its thermal decomposition generally gives free radicals, thereby leading to chain branching and auto-catalytic oxidation. Inevitably, peroxides in un-inhibited PAO oil are formed during transport and storage. The peroxide formation, in some cases, promotes discoloration that is unacceptable for critical products such as food-grade lubricants and turbine oils. Because of this, to evaluate the peroxide effect on oxidation stability and discoloration, a series of IP and ASTM color determinations was made on pre-aged PAO batches containing various levels of peroxide. The pre-aging was done by placing 500 grams of PAO oil sample in a 1000 ml. beaker and storing it in a convection oven at 100°C. The sample was taken on a daily basis for the determinations of peroxide numbers (ASTM D3703).

Fig. 2, representing the IP of PAO-1 oil at 180°C as a function of peroxide number in a semi-log plot, shows the IP decreases gradually as the peroxide number increase up to 10 ppm and then falls rapidly with increasing peroxide number. As illustrated in Table 2, similar trend in discoloration is observed in a 150°C oven aging test, showing that ASTM color rating increases relatively slowly with increasing peroxide number and then quickly with further increase.

Small amount of an aminic antioxidant (p,p'-di-tert-octyldiphenylamine, DODPA) was introduced in attempting to slow the formation of peroxides down. Test results, given in Fig. 3, show that PAO-3 oil can be stabilized with 10 ppm of DODPA for ten days and with 50 ppm for over 20 days. Im-

**Table 2. Discoloration of PAO-2 Base Stock Having Different Peroxide Number under at 150°C Oven-Aging Test (no antioxidant added)**

Test Oil	Initial Peroxide Number, ppm	ASTM Color (ASTM D1500)		
		0 hr	120 hr	240 hr
1	<1.0	L0.5	L2.0	L2.5
2	<1.0	L0.5	L2.0	2.5
3	2.3	L0.5	L2.0	2.5
4	3.7	L0.5	L2.0	2.0
5	9.6	L0.5	L2.5	3.0
6	19.7	L0.5	L3.5	4.0
7	27.6	L0.5	2.5	L4.0
8	50.3	L0.5	3.5	4.5



**Fig. 3. Peroxide Formation for PAO-3 Under a 100°C Oven Aging Test.**

provement in discoloration was also noticed, even though not reported here. In actual practice, it is highly recommended that a small amount of oxidation inhibitor into PAO base oils as well as other lube base stocks including severely hydroprocessed oils be added to reduce peroxide formation and discoloration.

### 3-2. Effect of Bromine Number (ASTM D1159)

In examining the bromine number effect on oxidation stability, a series of PAO base oils with different bromine numbers (unsaturation) was prepared in the laboratory and tested in the PDSC at 170, 180 and 190°C.

A summary of test results is given in Table 3 and graphically presented in Figs. 4 through 6 by plotting IP against bromine number in a semi-log chart. It is apparent from Figs. 4 and 5 that the IP changes exponentially with the bromine number, slowly at first with increasing bromine number up to 10 and rapidly beyond. This pattern is more dramatic for PAO-3, as shown in Fig. 6, in which the IP starts a rapid decline when the bromine number approaches 3.5.

To illustrate the difference in the declining pattern, the normalized ( $[IP]/[IP]_0$ , where  $[IP]_0$  is induction period at near zero bromine number) curves for PAO-1, -2 and -3 oils at 170°C are presented in Fig. 7. Results show that a heavier viscosity oil, PAO-3, is more sensitive toward the variation of bromine numbers than a lighter viscosity oil, PAO-1. A cause of the difference, though unclear at this time, may have been due to the fact that bromine number is presented by weight ratio, rather than by mole ratio. Molecular weight of the base oils are being determined using a GC method and additional work is needed to clarify this. Also, another difference noted is the IP of the three PAO oils at low bromine

**Table 3. Induction Period of PAO Base Fluids - Effect of Bromine Number**

	PAO Base Fluids*											
	PAO-1					PAO-2				PAO-3		
	A	B	C	D	E	F	G	H	I	J	K	L
Bromine Number	35	19.5	10	2.0	0.0	13.0	9.0	2.5	0.2	4.6	2.7	0.6
DSC-IP, min												
@170°C	7.5	-	41.8	49.5	51.5	17.8	47.5	57.0	60.5	47.3	59.5	64.3
@180°C	4.0	15.5	21.3	24.0	25.0	8.8	23.3	27.3	29.5	22.0	27.8	29.0
@190°C	2.4	-	9.8	10.8	11.3	-	10.5	12.5	13.3	10.3	13.3	13.8

\*Base fluids inhibited with bisphenol at a concentration level of 0.25 percent by weight

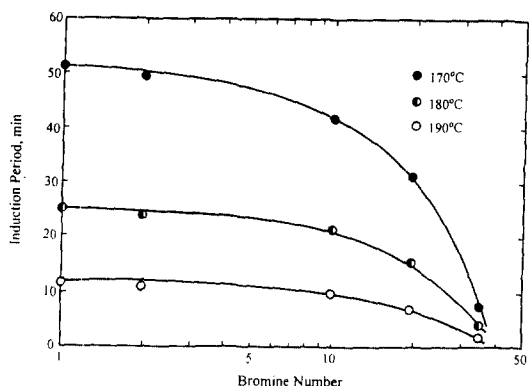


Fig. 4. Induction Period of PAO-1 Oil as a Function of Bromine Numbers.

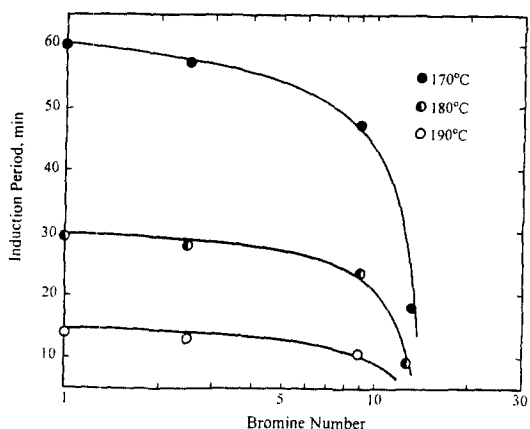


Fig. 5. Induction Period of PAO-2 Oil as a Function of Bromine Numbers.

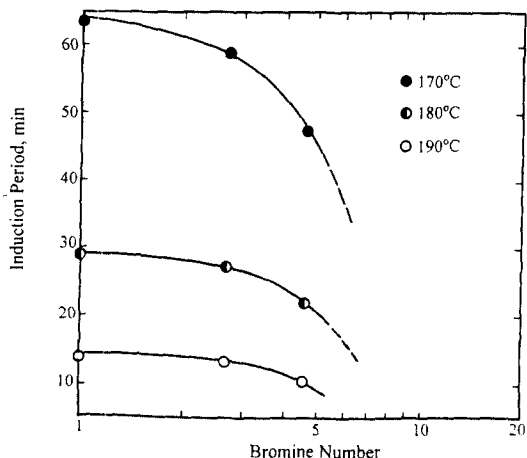


Fig. 6. Induction Period of PAO-3 Oil as a Function of Bromine Numbers.

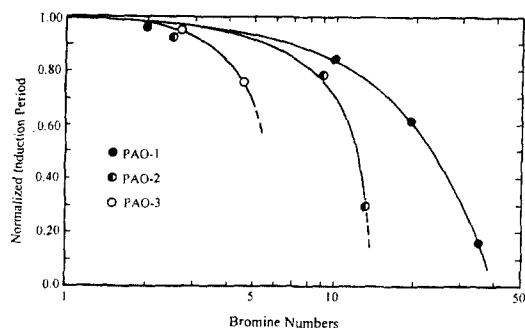


Fig. 7. Normalized Induction Period of PAO-1,2 and 3 Oils as a Function of Bromine Numbers (Oxidation Temperature=170°C).

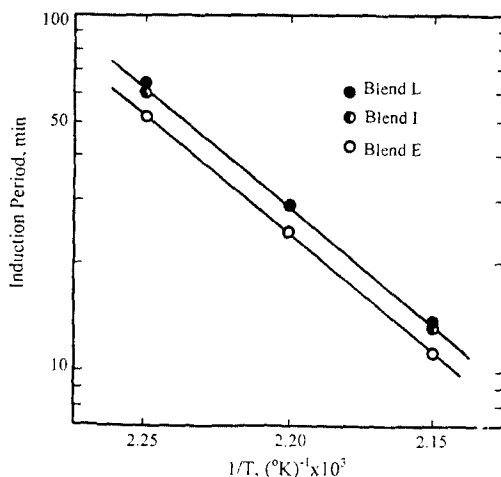


Fig. 8. Relationship Between DSC-Induction Period and Reciprocal Absolute Temperature.

numbers, the higher the viscosity, the greater the induction period. This difference may be related to possible difference in the diffusion rate of oxygen at high temperatures.

### 3-3. Effect of Temperature

With the aid of Table 3, Arrhenius equation is presented in Fig. 8 to characterize

$$[IP] = Ae^{-E/RT} \tag{1}$$

the activation energy E for PAO oils. The [IP] values used for discussion are from Blend E (PAO-1), I (PAO-2) and L (PAO-3) shown in Table 3. Straight lines are established and computed activation value is about 30.9 Kcal/gmole for all three oils. As expected, the IP is markedly reduced as the

oxidation temperature rises. The average reduction ratio for every 10°C temperature rise,  $\left. \frac{(IP)_{T_2}}{(IP)_{T_1}} \right]_{\Delta T=10}$  is approximately 0.48. This result confirms the well-known rule for estimating the oxidation rate of lubricants; i.e. oxidation rate doubles for every 10°C temperature increase.

### 3-4. Effect of Antioxidant Concentration.

A study with PDSC in this section is aimed at examining the effect of antioxidant concentration by blending PAO-2 having 9.0 bromine number with the bisphenol at different concentration levels. The induction period was determined at 170, 180 and 190°C.

It has been well-known from the kinetics of lube oil oxidation that the induction period of inhibited oils is related to inhibitor concentration in the following form:

$$[IP] \propto \sqrt{(IH)_0} \quad (2)$$

where  $(IH)_0$ =initial inhibitor concentration. Accordingly, in order to aid discussion of the inhibitor concentration effect, the induction period is plotted against the square-root of initial inhibitor concentration, which is shown in Fig. 9.

Three isotherms in Fig. 9 are straight lines, indicating that the induction period is directly proportional to the square-root of inhibitor concentration. Their slopes,  $\frac{\Delta[IP]}{\Delta\sqrt{(IH)_0}}$  are 79, 38 and 18.5 for the

170, 180 and 190°C isotherms, respectively. It is interesting to note once again that the average reduction ratio of the slopes for every 10°C increase in the oxidation temperature is 0.48. Such a good agreement between this and  $\left. \frac{(IP)_{T_2}}{(IP)_{T_1}} \right]_{\Delta T=10}$  values may

be fortuitous. Nevertheless, this agreement reaffirms that the oxidation life of lubricants is halved at every 10°C rise. Also, it is of interest to speculate if this 2 : 1 relationship remains unchanged for other oxidation inhibitors. But, should a combination of two or more antioxidants is used, this relation probably may not stand because of their potential synergistic or antagonistic activity. More information on this aspect would be of great value to comprehend the activity and effectiveness of antioxidants currently used in PAO-based fully for-

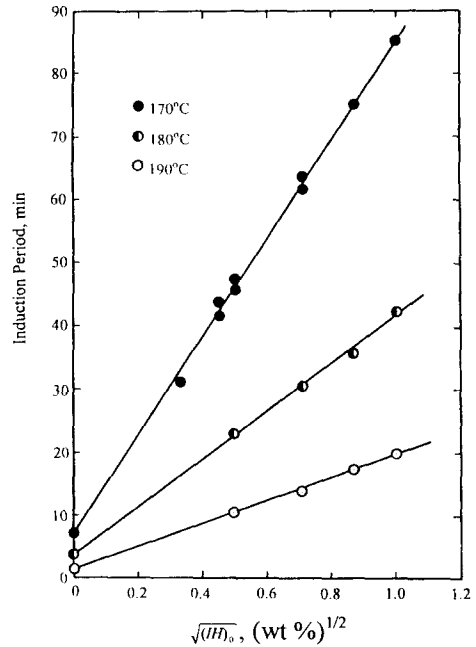
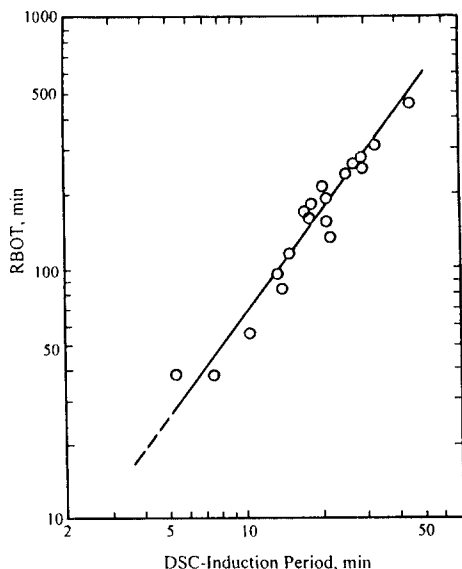


Fig. 9. Antioxidant Concentration Effect on Induction Period of PAO-2 Oil.

mulated synthetic lubricants.

### 3-5. PDSC versus RBOT

Rotary Bomb Oxidation Test (ASTM D2270) has often been used as a quality control test for many industrial lubricants such as turbine, air compressor and hydraulic oils. This includes fresh oils as well as used. It is, therefore, of some interest to investigate how PDSC data correlate with RBOT on inhibited PAO oils. Toward this end, PAO-1, PAO-2 and PAO-3 oils having different bromine and peroxide numbers were blended with the bisphenol at varying concentration levels. The 19 blended samples were subjected to PDSC at 180°C and RBOT for comparison. Test results, presented in Fig. 10, give a straight line relationship, indicating excellent correlation between the two tests. This relation also suggests that the oxidation characteristics of PAO oils blended with the bisphenol is unaffected by presence of water or hydrolysis. Thus, the PDSC is able to predict the comparative RBOT performance level of PAO oils. This prediction would hold as long as the presence of water in RBOT does not come into playing a key role in the overall control of oil oxidation processes.



**Fig. 10. RBOT Values as a Function of DSC-Induction Period.**

#### 4. Conclusion

The PDSC method described herein can amply differentiate the oxidation performance quality of

PAO oils containing varying levels of unsaturates and peroxides. It has proven to be repeatable, simple to operate and requiring a small test sample. Accordingly, the method can be used with great confidence as a quality control test for PAO oils at manufacturing and blending plants. Moreover, the PDSC method is versatile enough to be used for kinetic and related studies on the oxidation of inhibited lube oils. Also, it appears to predict RBOT performance of inhibited PAO oils.

#### References

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