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The development of a standard method for determining oxidation induction times of hydrocarbon liquids by PDSC ☆

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Abstract

The use of oxidation induction times (OITs) of hydrocarbon fluids in predicting oxidative stability has long been of interest to the thermal science community. This statistical study is based on previous work where parameters such as heating rate, temperature, pressure, and sample size were optimized. Here, two reference oils, A and B, and two procedures were investigated and compared on the basis of OIT variability. Calorimeter pan types were also compared. The pans were all made of aluminum but differed in shape, size, surface topology, and contamination species. The effects of these variables on OIT were investigated, and pan characteristics were studied using scanning electron microscopy and energy dispersive X-ray spectroscopy. This study will provide specific parameters to enhance data quality, a simple production method that is easy to implement and data that are easy to interpret. Finally, a precision and bias statement of the final protocol will be developed through a national ASTM round-robin study.

Keywords: Bias; Calorimeter pan; Hydrocarbon; Oil; OIT; PDSC; Precision; Stability

1. Background

A previous investigation of the oxidation method resulted in a round-robin study (1990, 1991). A number of labs were sent reference oil A and a supply of flat shallow pans to test the proposed ASTM oxidation method, E37.01.10A [1]. The

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data generated by these labs spread over a 16 min range in measured oxidative induction times (OITs). The usual variables in developing an oxidation test of this type are temperature and pressure of the calorimeter cell, heating rate, gas flow, sample size, sample pan type, and reference oil. Two procedure were compared in this study, and the variables were narrowed to an investigation of the reference sample and the pan type by means of a statistically designed study (1991).

2. Experimental design

Two methods were investigated in this study: one was developed by Dr. Rhee of Army Research [2] and the other was proposed by the ASTM E37 committee. Both utilize a pressure differential scanning calorimeter (PDSC) with the heating profile of a 40°C min^{-1} ramp to 175°C with an isothermal hold at 175°C until oxidation occurs. Both methods also require the isotherm to occur under 500 psig of oxygen with an oxygen purge through the PDSC cell.

The differences between the two methods lie in the time at which oxygen is introduced into the reaction cell, and in sample sizes and flow rates. The Army procedure requires 2 mg of sample in an SFI pan, and oxygen enters the cell at the onset of the 175°C isothermal hold with a 100 ml min^{-1} gas flow. The proposed ASTM procedure uses 1 mg of sample, and the cell is equilibrated at 500 psig with 25 ml min^{-1} flow before the test start. For each method, oil B in two pan types, a flat aluminum pan and an SFI pan, underwent oxidation. Each combination was repeated four times with OITs being measured each time.

To examine the differences in oxidative properties between the two reference oils, both samples underwent oxidation with both proposed methods. Both flat aluminum pans and SFI pans were utilized in each procedure. Again, each combination was repeated four times and OITs were measured.

This study also includes comparison of six aluminum pan types. One pan type is made of anodized aluminum which is coated with a chromium component. The remaining five pan types are made of untreated aluminum, either pressed or milled into their respective shapes and sizes. Each pan was cleaned by rinsing with methylene chloride followed by acetone and finally blowing the pan dry with nitrogen. One milligram of oil A was used in the ASTM method and OITs were measured and compared. Three runs were performed with each pan type. Scanning electron microscopy (SEM) enabled us to view the surfaces of each pan and energy dispersive X-ray spectroscopy (EDX) measured the amount of surface contamination.

3. Results and discussion

3.1. Method and reference oil data

To compare methods along with reference oils, OITs were measured for each reference in both methods using SFI and regular aluminum pans. The average OIT

Table 1
Average OITs and standard deviations for each data set of four runs

Method	Oil	Pan type	Oxidative induction times in min	
			Average	Std. dev.
ASTM	A	SFI Regular flat pan (1)	21.39	2.89
			21.95	1.09
	B	SFI Regular flat pan (1)	45.67	1.74
			46.65	1.88
Army	A	SFI Regular flat pan (1)	36.09	5.54
			35.00	5.54
	B	SFI Regular flat pan (1)	49.41	1.02
			48.19	2.99

and standard deviation for each data set of four runs are listed in Table 1. From this data set, comparisons may be drawn for the methods as well as for the references oils. Comparing methods statistically, the ASTM procedure yields slightly lower standard deviations on average in the oxidation induction times than does the Army procedure. The Army method could also lead to larger data variation through analyst error. This method requires the analyst to introduce oxygen into the PDSC cell exactly when the temperature begins the 175°C isotherm, and the analyst may miss the exact time when that temperature is reached. For consecutive runs, oxygen may be introduced to the chamber at different points of time in respect to the 175°C onset, which would result in a noticeable deviation in the oxidation induction times. The ASTM E37 method requires that the reaction cell be stabilized at 500 psig oxygen before the test is started. For consecutive runs, this method does not introduce further variation from the gas introduction event into the PDSC cell.

Runs performed repeatedly with reference oil B show a lower standard deviation than those of oil A. Both are diluted motor oils; however, the OIT for oil B is twice that of oil A (Fig. 1). These oils were chosen on the basis of engine test performances in which the amounts of sludge, varnish, wear, and viscosity change during the test, all being effects of oil oxidation. In the engine test, oil B earned a higher pass rating that oil A, meaning that the antioxidant of oil B is more efficient than that of oil A, so the oil package becomes a more stable one. The standard deviations illustrate this fact in that the OIT for B displays less variation run to run. And for round-robin purposes, results from independent labs would also be in better agreement than in previous studies.

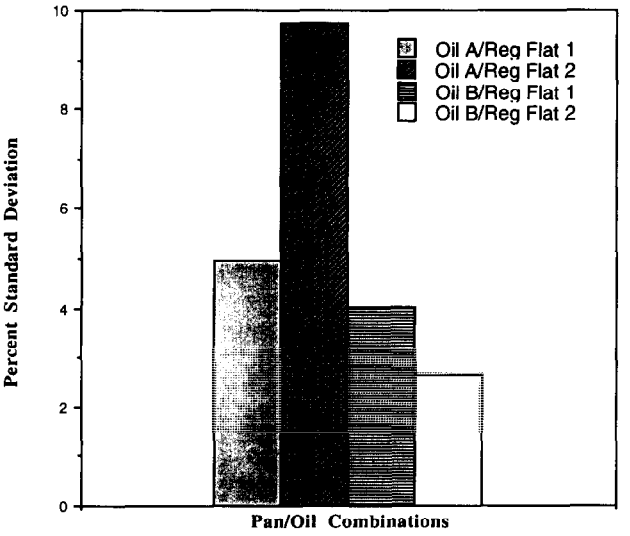

Fig. 1. Variations of two reference oils run in two different pan types.

3.2. Pan type data

To compare the PDSC sample pans, parameters for the ASTM procedure were utilized, i.e. 1.00 mg sample weight; open pan, 500 psi oxygen at a flow rate of 25 ml min^{-1}, heating rate of 40°C min^{-1} to 175°C, and isothermal hold at 175°C. Three runs were made with each pan type and results are listed in Table 2. The anodized pan is coated with a chromium substrate that causes the pan surface to appear cracked and possibly increases surface area for reaction (Fig. 2). The chromium is confirmed via EDX, and the OITs and standard deviations prove to be fairly low. The low OITs for this pan type could result from either the increased reaction area or from the chromium acting as a catalyst in the oxidation scheme.

Table 2
Results for three runs with each pan type

Pan type	Average OIT in min	Standard deviation	Contaminants (by EDX)
Anodized hermetic pan	9.6	0.8	Cr
SFI pan	21.4	2.9	Fe
Hermetic pan	17.3	2.8	–
Shallow flat pan	29.2	1.5	Ca
Regular flat pan (1)	22.0	1.1	S, Cl, K Ca, Na, Mg
Regular flat pan (2)	16.6	0.4	–

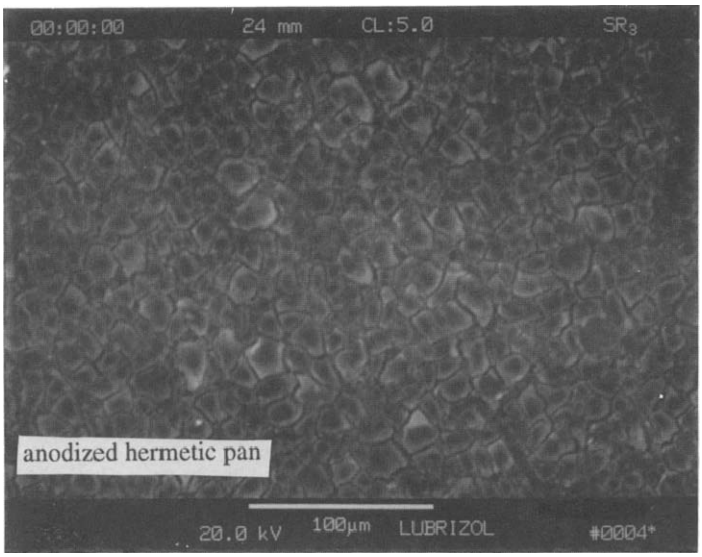

Fig. 2. Anodized hermetic pan; scanning electron micrograph, original magnification 300×.

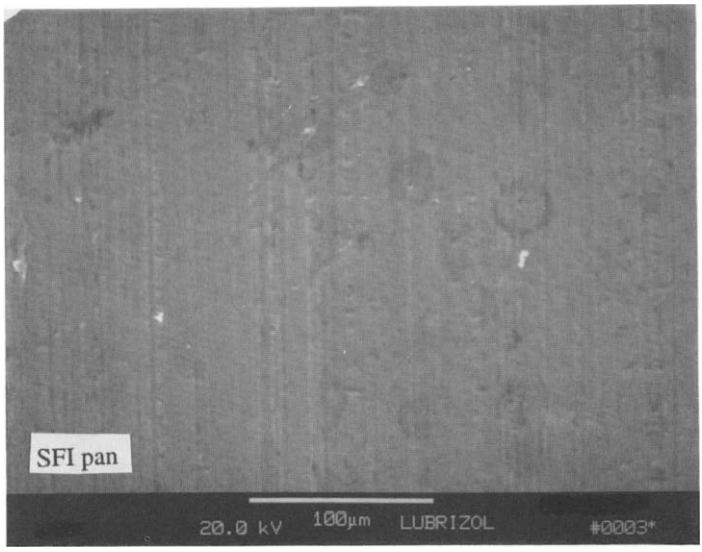

Fig. 3. SFI pan; scanning electron micrograph, original magnification 300×.

OIT results for the SFI pan illustrate the highest standard deviation. EDX for these pans show some iron contaminants which could contribute to the variation in induction times. SEM shows that the pan surface is slightly ridged (Fig. 3), with a non-homogeneous surface pattern (there are dark spots on the surface). The aluminum hermetic pan shows no apparent contaminants through EDX spectra, and the standard deviation in OITs is relatively high. SEM shows blemishes present

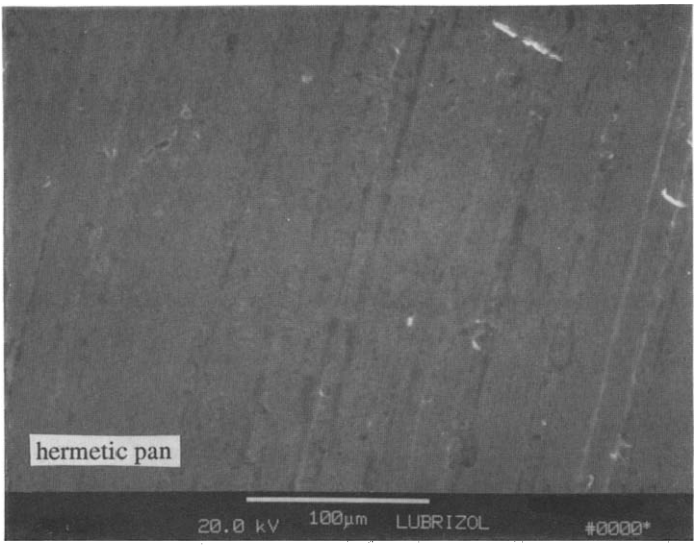

Fig. 4. Hermetic pan; scanning electron micrograph, original magnification 300×.

on the surface (Fig. 4), but EDX indicates that these are probably aluminum. The shallow flat pan, displays large amounts of calcium, e.g. $CaCO_3$, on the surface, but the standard deviation is fairly low. This is a relatively small pan with less reaction area than the other untreated aluminum pans, and a higher OIT could result. The high OIT could be further explained by the presence of calcium (Fig. 5), which might be serving as an inhibitor in the oxidation process.

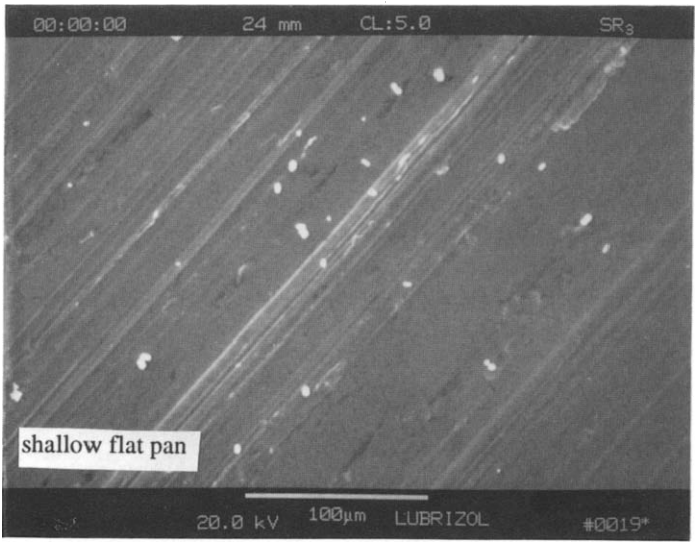

Fig. 5. Shallow flat pan; scanning electron micrograph, original magnification 300×.

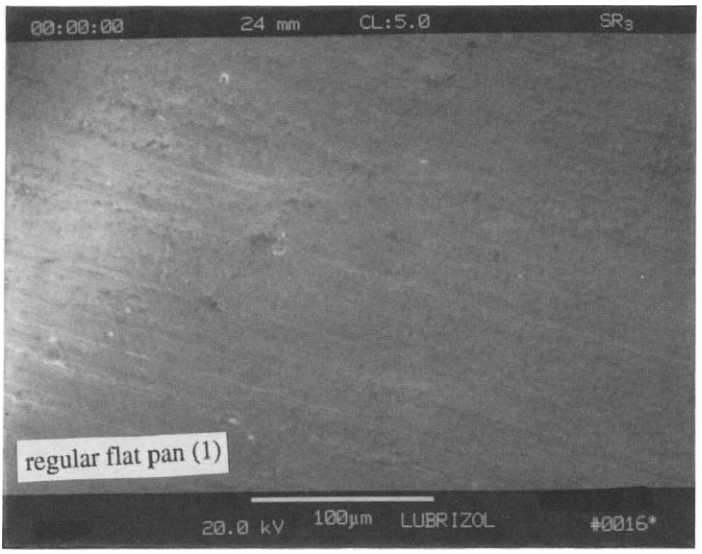

Fig. 6. Regular flat pan (1); scanning electron micrograph, original magnification 300×.

The pan type displaying the lowest standard deviation is the regular flat aluminum pan. This study investigated a flat pan from two separate vendors, and each vendor supply yielded induction time variability. The pan from vendor one contains a number of contaminants, but these do not seem to affect adversely the oxidation process, as measured by induction time. The surface of this pan appears to be homogeneously corrugated with no visual defects, as shown by SEM (Fig. 6). The pans from the second vendor displayed even more favorable results. The standard deviation was the lowest for all pans studied while the surfaces of the pans are very flat and clean, with no contamination (Fig. 7).

4. Conclusions and recommendations

In the development of an ASTM oxidation procedure, any further round-robins would require that all labs follow and document a supplied protocol. The ASTM E37.01.10A method would allow for fewer analyst inconsistencies than would the Army procedure developed by Dr. Rhee. This ASTM method, modified to use reference oil B along with a flat aluminum pan, would be the best choice for a round robin. These parameters have consistently displayed the lowest standard deviation in oxidation induction times.

In selecting a pan type for oxidation studies, normally litle attention is paid to specific pan characteristics. However, these characteristics play an important role in the variability of oxidation results, as observed through induction time. The regular flat aluminum pan types display little variation in OITs and they have median induction times.

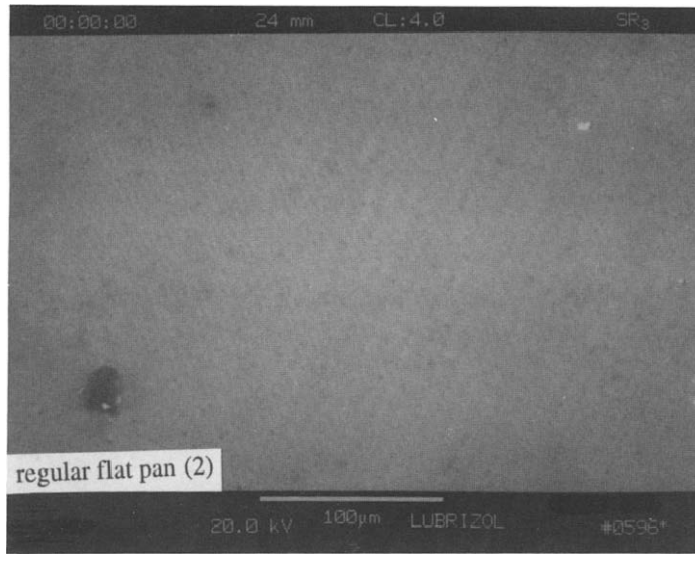

Fig. 7. Regular flat pan (2); scanning electron micrograph, original magnification 300×.

Should a pan display a short induction time, as is the case with the anodized pan, resolution is lost. System changes arising with time or experimental error would not significantly alter such a low induction time. Changes to the system might be overlooked. The median induction times with low variability displayed by the regular flat aluminum pans provide an effective parameter for monitoring the system.

An additional round-robin study with at least ten labs should test these parameters. Alternate samples should be tested along with reference oil B to validate the scope of the test parameters. Not only should the labs report the results, but also document the method they use so that we may note any inconsistencies in procedure.

References

[1] Project Document for ASTM E37 Committee for Project TM-01-10A-10, Standard Method for Determining Oxidation Induction Time of Hydrocarbons by DSC, January, 1991.
[2] In-sik Rhee, National Lubricating Grease Institute, 55 (1991) 4.