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OXIDATIVE STABILITY OF LUBRICANTS MEASURED BY PDSC CEC L-85-T-99 TEST PROCEDURE

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The CEC L-85-T-99 pressure differential calorimetry (PDSC) test was developed in Europe for ACEA E5 specification for heavy duty diesel oils. This test differentiate between base oils, additives, indicates synergies between antioxidants and correlates with other oxidation tests. Occasionally, the PDSC test can have difficulties to provide a true value for the OIT, which can vary between samplings. This work gives evidence of such case and concludes that variability in results is caused by variability in the oil rather than in the test itself. It appeared possible that certain oils might not be fully homogenous and this could produce a problem for representative PDSC sampling.

Keywords: *lubricants, oil oxidation, oxidation tests, PDSC thermal analysis*

Introduction

The main function of the engine oil lubricant is to extend the life of moving parts in the engine which operate under many different conditions of speed, temperature, pressure and atmosphere. The internal combustion engine is a powerful chemical reactor for catalysing the process of oil oxidation with engine metal parts, such as iron and copper, acting as effective oxidation catalysts. Therefore good resistance to oxidation is probably the most important requirement of a lubricating oil.

The base stocks used for lubricants are hydrocarbons containing mainly paraffins and smaller quantities of naphthenes and aromatics. Traces of nitrogen, sulphur and oxygen containing heterocycles, together with mercaptans, thioethers and disulfides are an integral part of Group I and II base oils. If the ratio of aromatics and sulfur is at its optimum level then the natural oil resistance to oxidation is also maximised [1]. Rasberger's studies [2] concluded with the mechanism and factors influencing the degradation processes taking place in lubricants.

While a long time ago the natural level of protection against oxidation of base oils was adequate, now it does not fulfil the requirements and it has become necessary to develop stabilizers against oxidation which would extend the useful life of lubricant. An excellent compendium of types of antioxidants can be found in Lubricant Additives [3]. In this book, in the chapter designated to oxidation stabilizers, one can find the mechanism, types of antioxidants and their synergistic effects.

Oxidative degradation of lubricants can be divided into two classes of reaction – bulk oxidation and thin film oxidation. Bulk oxidation usually takes place in the cooler areas of the engine such as the sump and is caused by an attack of oxygen, blow-by gases and other materials generated during combustion. These processes cause oil thickening due to polymerization of hydrocarbons from the base oil and additives. The presence of acidic species also leads to an increase in the acid number (AN) which could induce corrosion. Thin film oxidation describes the class of reactions that occur in the piston zone (ring, grooves and lands), where temperatures are high and the residence time of the oil is quite short. Under those conditions the acidic compounds are decomposed leading to deposit formation.

Careful selection of base oils and additives lead to the formulation of lubricants of specific properties and increased resistance to oxidation. The best way of testing those properties is an engine test. Some engine tests evaluate the oil tendency to thickening (Sequence IIIE, PSA TU5, VW T4) and others evaluate high temperature thin film deposits (OM 364LA, OM 441LA, Caterpillar 1P/1Q). However engine tests are long and expensive and therefore formulators are looking for alternatives in screen testing.

A number of laboratory screen tests already exist, but each one of them evaluates only a limited aspect of lubricant performance and not the overall performance in the engine. There are therefore attempts to combine several bench test results into a model [4] which could predict the engine performance. Alternatively attempts are made to imitate the engine performance by new bench test designs in which a better

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comparison with engine tests could be achieved in one test [5]. In the early nineties a pressure differential scanning calorimetry (PDSC) method was developed to evaluate the thermal and oxidative stability of oils [10]. The method included a temperature ramp, 100 psi oxygen pressure, steel pans with lids and vent pinholes. The curves consisted of two peaks and their ratio was used as the index for deposit forming tendency of the oil. Further studies indicated good correlation with engine tests [11]. Also a PDSC test run in isothermal conditions was developed and described as ASTM D 6186 test [13].

CEC L-85-T-99 test procedure

PDSC attracted the attention of Association des Constructeurs Européens de l'Automobile (ACEA). This method could provide the meaningful data on thin film oxidation of the lubricant and therefore could be a predictor of its behaviour in heavy duty engines like OM 364LA and OM 441LA. CEC L-85-T-99 test was developed [6] and was included in ACEA E5 specification.

CEC L-85-T-99 is an easy to use, rapid test requiring a very small sample volume. Repeatability and reproducibility of CEC L-85-T-99 test, run on two reference oils RL133 and RL134, is generally acceptable and ACEA E5 limit of acceptance is >35 min OIT (oxidation induction time). In November 2004 the new ACEA E7 specification will be issued and PDSC test will continue to be included without changes to the procedure.

A characteristic index for the oxidation stability is the OIT, which is defined by the time between the start of exposure to oxygen and the onset of the exothermic reaction in isothermic conditions. The prime parameter in this time determination is the amount of oxygen supplied. This can be regulated by the use of air or oxygen and further by increasing the pressure of those gases. Pressure is proven to be the most important parameter of the test [8]. Another parameter is temperature followed by the temperature ramp rate, cell and pan quality and cleanliness. Method for analysis of results and inherent features of the instrument are also of importance. Summary of test conditions is collected in Table 1.

Investigations and test results

While it is not the objective of this paper to elaborate on CEC L-85-T-99 test method development or its repeatability and reproducibility, it is worth mentioning what information about lubricants can be obtained from the test results.

Table 1 Conditions of CEC L-85-T-99 test procedure

Air atmosphere	100±7 psi, 690±47 kPa
Sample size	3.0±0.2 mg
Pan	Seiko aluminium
Flow rate	Static, no flow
Initial calorimeter temperature	<45°C
Equilibrating temperature	50±5°C
Temperature ramp rate	40±10 K min^{-1}
Isothermal temperature	210±2°C
Test duration	120 min maximum <(after isotherm)

Differentiation between base oils

The same set of additives was mixed at the same level with base oils of different origin and submitted to the PDSC test. It can be seen from the overlaid plots in Fig. 1 that differentiation between base oils is very clear and in agreement with the improving quality of oil:

Group I (27 min)<Group II (36 min)<
<Group III (42 min)<Group IV (57 min)

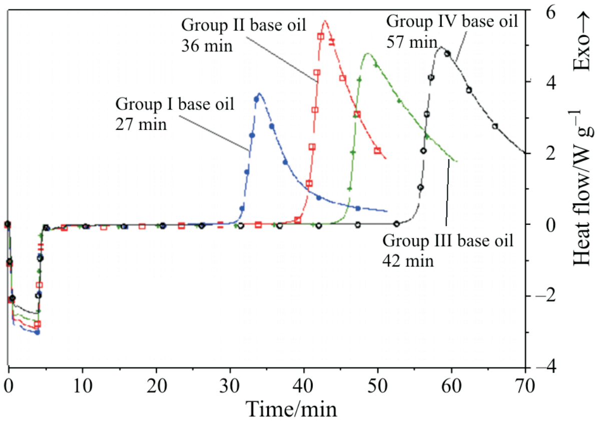

Fig. 1 Overlay of PDSC curves with base oil as the only variable in lubricant's composition (PDSC ACEA test OIT at 20°C/100 psi)

Group I base oils may contain more than 10% unsaturated molecules which include aromatic and heterocyclic formations prone to oxidation. Group II base oils are more than 90% saturated and contain only traces of sulfur. Group III base oils are products of specific hydrocracking/isomerization process and are practically 100% saturated. Group IV base oils are products of alpha-olefins oligomerization in a controlled process yielding 100% homogenous paraffinic product after final hydrogenation. The basic differences between oils are collected in the American Petroleum Institute base oil classification table (Table 2).

Table 2 API base oil classification table

Base oil category	Sulfur/%	Saturates
Group I	>0.03	<90
Group II	≤0.03	≥90
Group III	≤0.03	≥90
Group IV	0	100

It has been reported that the PDSC test could identify the changes in the final hydrogenation process of polyalphaolefins [7] (PAO – Group IV bas oils), which confirms our experimental data. Investigation of differences between Group III oils from various manufacturers can also be evaluated by PDSC test. In Fig. 2 three different Group III oils (A, B and C) are compared with lubricants based on Group IV and Group I oils. Although here the results are not significantly different, the gradation of thermal stability can be observed.

Differentiation between detergents

Differentiation between detergent chemistries was easily obtained when comparative testing was conducted on fluids with detergents added to the same value of base content. In each group aminic antioxidant was always at 0.15% level, while phenolic antioxidant was increased from 0 to 2.0%. PDSC test results indicate, as seen in Fig. 3, that sulfonate detergents, not having own properties to suppress the oxidation, show only the effect of added antioxidants. Phenates, due to their phenolic group, can act as antioxidants, and indeed, a considerable improvement is seen in OIT when compared with sulfonates. The strongest as antioxidants, salicylate detergents, outperform by far the phenates and improve OIT even when low level of antioxidant is present. The high results, exceeding the upper test boundary (120 min), which could make them slightly less reliable, are also masking the effect of phenolic antioxidant.

Similar observations were reported with zinc dialkyl dithiophosphate (ZDDP) investigated in PDSC test [9]. ZDDP is used in lubricants as an antiwear/antioxidant agent. Reported obtained data showed differences between oils containing the same additive at different concentrations and among oils containing a single additive and the mixture.

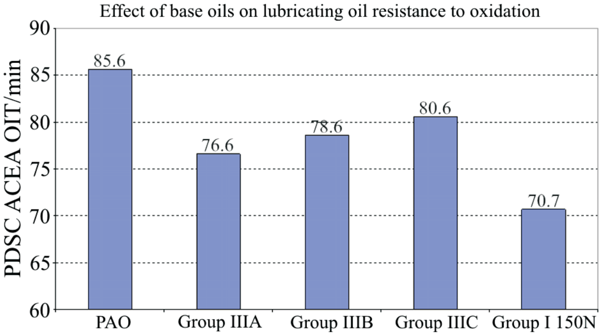

Fig. 2 Comparison of three different Group III oils with Group I (150N) and Group IV (PAO)

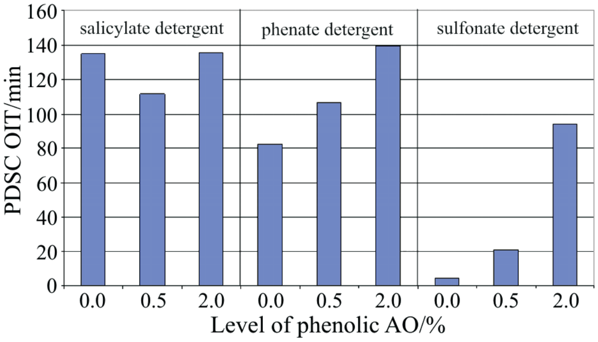

Fig. 3 Comparison of OITs obtained on formulations containing three different detergents as the only variable (PDSC ACEA 210°C)

Differentiation between antioxidants and their synergisms

Many publications were written on the mechanism and synergism of phenolic and aminic antioxidants. A simplified and convincing mechanism was presented by Gatto and Grina [12] who stated that hindered phenols and resulting phenoxy radicals are more stable than the analogous amines and amino radicals. The phenolic antioxidant simply acts as a proton source for the more reactive amine. Under ideal conditions, low levels of amine relative to phenolic antioxidant are required for optimum synergism by this mechanism.

In testing of this synergism using CEC L-85-T-99 test procedure similar observations were made. 14 experimental oils were blended according to composition listed in Table 3.

PDSC OIT test clearly differentiates between aminic and phenolic antioxidants and responds to their level in this prepared matrix of oils. Also the synergistic effect of mixed antioxidants can be observed, as seen in Fig. 4.

Additionally it has been observed that CEC L-85-T-99 test shows excellent response to the total addition of antioxidants, as represented in Fig. 5.

CEC L-85-T-99 compatibility with other oxidation tests

Some papers [4, 9] in which PDSC technique was investigated alongside bulk oxidation tests, reported good correlation between them. In this respect CEC L-85-T-99 test is no different from other PDSC methods and from our testing carried out we can find the correlation with bulk oxidation tests. Work conducted on five very different engine oil lubricants in

Table 3 Composition of oils with combination of aminic and phenolic antioxidants

Oil	1	2	3	4	5	6		
	0.15 amine	0.50 amine	0.15Ph	0.5Ph	1.0Ph	2.0 Ph		
phenolic AO	–	–	0.15	0.50	1.00	2.00		
aminic AO	0.15	0.50	–	–	–	–		
PAO6 base oil	99.85	99.50	99.85	99.50	99.00	98.00		
Oil	7	8	9	10	11	12	13	14
	0.15N/ 0.15Ph	0.15N/ 0.5Ph	0.15N/ 1.0Ph	0.15N/ 2.0Ph	0.5N/ 0.15Ph	0.5N/ 0.5Ph	0.5N/ 1.0Ph	0.5N/ 2.0Ph
phenolic AO	0.15	0.50	1.00	2.00	0.15	0.50	1.00	2.00
aminic AO	0.15	0.15	0.15	0.15	0.50	0.50	0.50	0.50
PAO6 base oil	99.70	99.35	98.85	97.85	99.35	99.00	98.50	97.50

Table 4 Results of DKA and PDSC oxidation tests generated on five different engine oils

Oil	A	B	C	D	E
			Characteristics		
Base oil	Group I	Group I/Group III	Group I	Group I/Group III	Group I
Total AO/%	1.3	1.3	2.3	2.3	0.5
Detergent type	sulfonate	sulfonate	sulfonate	sulfonate	sulfonate/phenate
			Bulk oxidation test (DKA/14 days at 170°C)		
Viscosity increase/%	2820	1615	1691	807	5000
			PDSC CEC-L-85-T-99		
OIT/min	105	120	114	126	26

terms of base oil, additives content and viscosity grade is summarized in Table 4. All oils were tested in DKA bulk oxidation test at 170°C and in PDSC test and good differentiation between oils was obtained in both sets of tests results.

Plotting the DKA test results versus PDSC produced the graph with excellent correlation of R^2=0.9, as seen from Fig. 6.

Since we are looking at capturing different oil properties in bulk oxidation and in thin layer oxidation, such good agreement between them might be

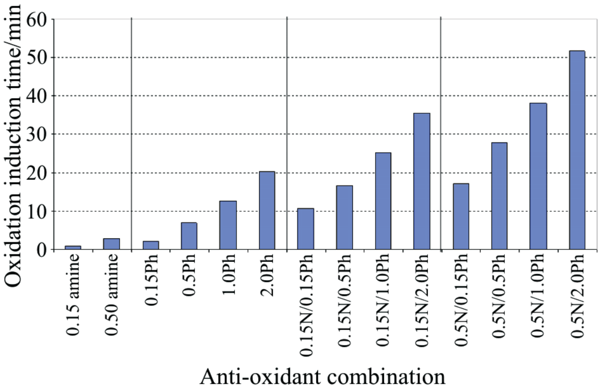

Fig. 4 Synergistic effect of phenolic and aminic antioxidants in lubricants as measured by CEC L-85-T-99 test procedure

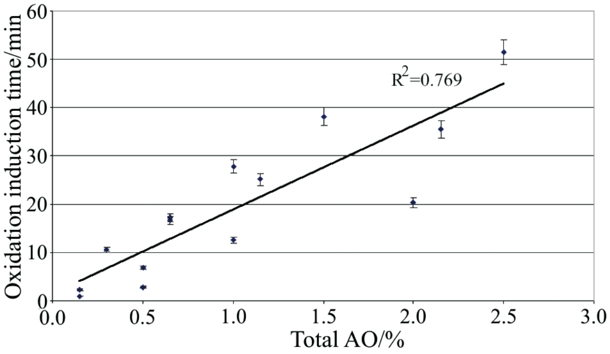

Fig. 5 PDSC OIT results as function of total antioxidant content

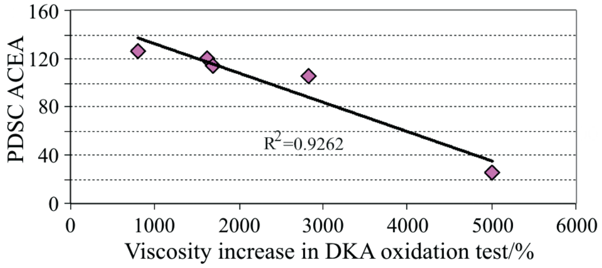

Fig. 6 Correlation of PDSC with viscosity increase in DKA oxidation test

somehow worrying and correlation to engine test results might remain questionable.

Technical issues of PDSC CEC L-85-T-99 test

Despite the problem of a more general nature mentioned above, that there is not much difference between testing bulk and thin layer oxidation, there is also a technical issue related to PDSC test which might affect the result and this is the oil sample size involved in testing.

The OIT result is the mean value of two runs which are less than six minutes apart. In the majority of cases the test is run twice in order to satisfy the conditions for taking the average. However some oils do not behave so well and they require extra runs to establish the true OIT.

An example of such case is the commercial oil which was run four times obtaining OITs of 70.17, 81.98, 83.02 and 71.68 min. Depending on the order in which these tests were carried out the results could have been submitted after two runs as either as 71 or 83 min whilst keeping to the test method. The oil was put on rollers for 72 h to mix thoroughly and tested again. The result was a time of 72 min. When tested in another laboratory, the final result obtained was 84 min. This means that the oil would either be accepted or not accepted by the specification, should the result be on either side of the required limit.

It has been suggested that the problem could be in poor mixing of the oil. Sampling for PDSC is only 3 mg, thus it is possible that there could be less AO molecules within one portion of tested oil than there is within the next. When the blend is made and all components are dissolved, it might not necessary mean that the oil is fully homogenised. The inherent thickness of the oil makes homogenisation more difficult.

The variability could also be related to the instrument, however it is calibrated once a month and no deviations were observed. As part of accreditation, reference oils RL133 and RL134 are run alternately every tenth sample, and no abnormalities were observed there either.

The PDSC cell consists of two heating plates with pans, the front pan contains the oil sample, whose heat flow is compared to an identical empty pan in the back position. Thus when a thermal event occurs in the oil it plots a graph of the heat flow relative to what is happening to the empty pan. If the pan locations are reversed then a negative signal is obtained, as illustrated in Fig. 7.

If two pans of equal sample size and identical oil were put into the cell in the front and back locations then the software would measure the thermal events of one pan against the other. If the oils were identical, they would oxidise simultaneously and the upward signal would cancel out the downward one and a flat line would be drawn. This would mean that any variation between runs would be an error with the instrument rather than variation in the oil.

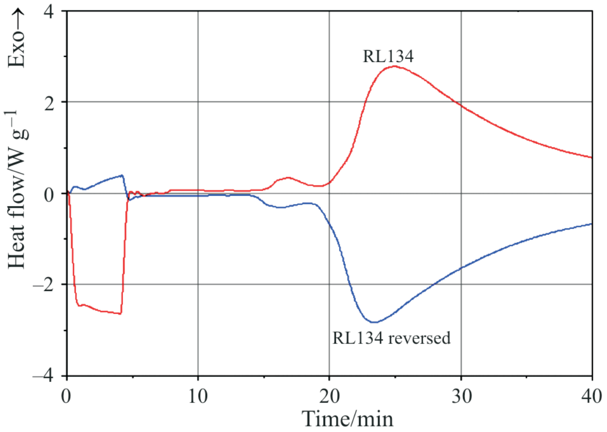

Fig. 7 Overlay of two reference oil runs, one in normal and one in pan reversed mode

However, if a plot of two pans showed a peak and a trough it would be due to the oil having variable oxidation induction times. Thus equal amounts of oil under the same test conditions give different OIT, and the oil rather than the instrument would be the cause of variability.

In order to eliminate any fluid inconsistency, pure PAO base oil with no additional components was put for test. Therefore there should be no variance in the composition of the sample taken. Into both pan locations an aluminium pan containing exactly 3 mg of oil was loaded with the flat plot as expected, Fig. 8.

As seen from the plot, there is minimal variance in the heat flow around zero W g^{-1} indicating that oxidation occurred at the same time for both oil samples. Run under the standard conditions PAO 6 has a typical heat flow of about 4 W g^{-1} showing that such small variance around zero is insignificant.

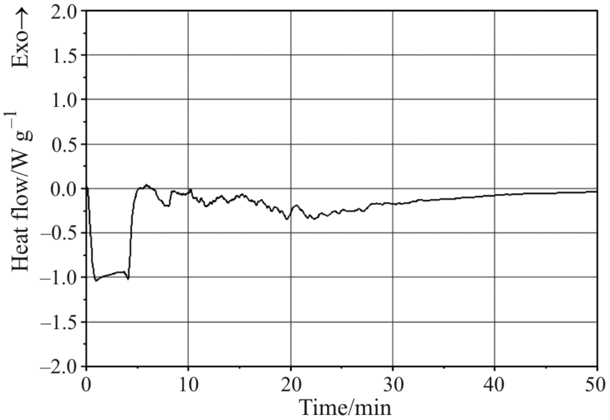

Fig. 8 Plot obtained when pans with sample were placed on both reference and sample positions

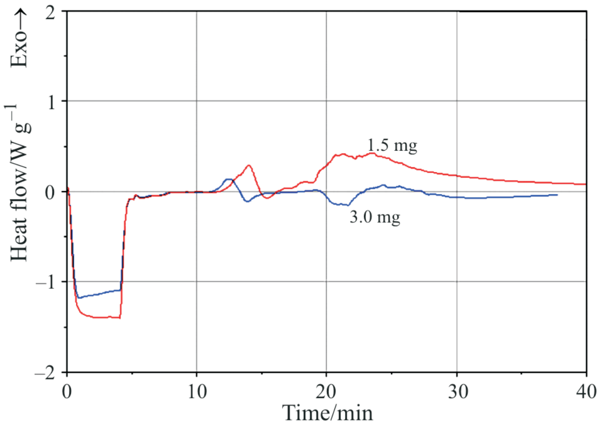

Fig. 9 Overlaid plots of two experiments, one with 3 mg and one with 1.5 mg of oil on each pan

The flat line resulting from component free base oil is to be expected, variation should take place when additive components are introduced into the oil. This hypothesis was tested using two equal sized samples of base oil. As the standard test uses 3 mg in one pan, two masses of sample were tried. The individual masses of oil were 3 and 1.5 mg (3 mg total). The reference oil RL134 was used in standard Al pans and loaded into the front and back positions. The OIT plots for both runs are overlaid in Fig. 9.

Being a reference oil, RL134 gives consistent readings of OIT of around 20 min and heat flow of around 4 W g^{-1} for a standard test. The plots in Fig. 9 show an almost flat line with a maximum peak of 5% of the heat flow normally observed on oxidation.

When overlaid with data from two RL134 runs (one standard, one standard with pan position reversed) the above plot can be explained. All three lines in Fig. 10 are the results of independently carried out tests. None are a transformation or addition of others. The blue line shows the normal pan configuration, and the red with pans reversed. The normal run has a slightly shorter oxidation induction time than the run with reversed pan positions.

Addition of the two signals for runs using one pan of oil (red and blue), leads to the form of the green line. This explains why the run with sample in both pans initially has a slightly positive signal, corresponding to a pre-peak in the oxidation of the oil in the front pan. When the back pan has its pre-peak the green line begins to decline until both exotherms are equal and green line returns to zero.

An example of the problem oil was run in two pans simultaneously and was compared with five runs in standard mode. The curve of oil simultaneously placed in two pans is different from other runs, as it closely resembles the standard run and shows the exothermic peak in the expected place, but much smaller, Fig. 11.

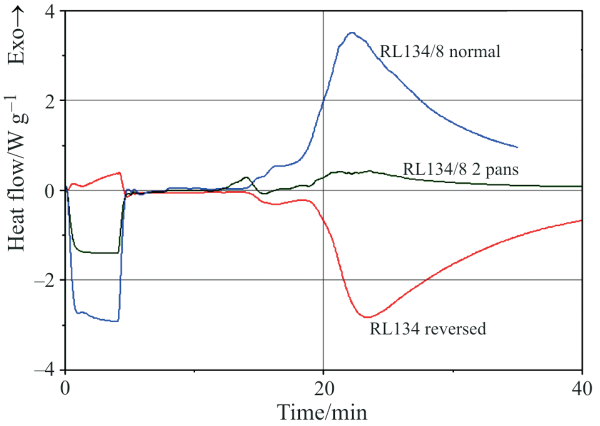

Fig. 10 Overlaid plots of three runs for RL134 reference oil standard, reversed and sample in both pans

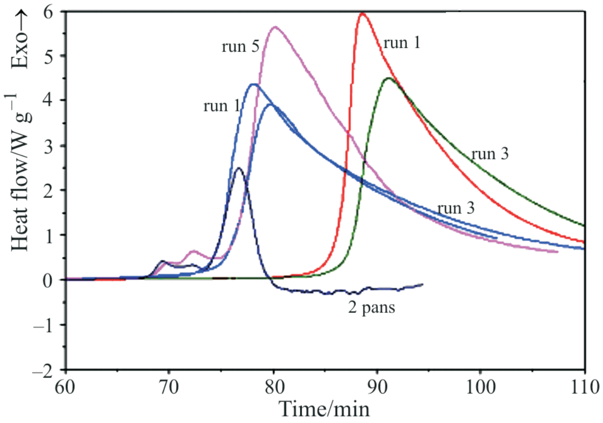

Fig. 11 Multiple plots of problem oil compared to plot obtained from experiment with oil in both pans

This may be because the front pan oxidises first causing the peak, followed by the back pan starting to oxidise with delay. This causes the two signals to cancel each other out leading to a peak of diminished height and width. The heat flows are approximately the same and cancel each other out effectively and the two-pan signal stabilises around zero value.

This shows that the variability in results for this oil is a result of variability in the oil rather than variability in the test itself. The base oil without additives and the reference oil both give ‘flat’ signals, yet a problematic oil gives a distinct signal as the heat flows of the two oils do not cancel each other out.

Conclusions

CEC L-85-T-99 test can be successfully applied to distinguish between different quality base oils and types of additives, particularly detergents and antioxidants.

This method is very responsive to the total antioxidants level, including additives with partial function as antioxidants and is able to detect synergisms between antioxidants.

It correlates well with other methods based on PDSC technique and other types of oxidation tests. Care must be taken in interpretation of this method data as related only to thin layer oxidation process.

Very small sample sizes might produce a problem in determining true OIT values due to the possibility of non-homogenous distribution of additives in the viscous environment of base oils and polymers present in the lubricant.

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