

## **DETERMINATION OF SPONTANEOUS IGNITION TEMPERATURES (SITs) OF AVIATION LUBRICANTS USING PRESSURE DIFFERENTIAL SCANNING CALORIMETRY (PDSC)**

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### **ABSTRACT**

The usefulness of pressure differential scanning calorimetry (PDSC) in studying spontaneous ignition temperatures (SITs) of selected aero-engine oils, hydraulic fluids and greases is shown. Dependence on heating rates, oxidative medium and sample pan material was studied.

### **INTRODUCTION**

Recently [1] we reported the DSC cell to be a versatile tool to study thermal-oxidative degradation of lubricants, especially synthetic neopentyl-polyol based oils for military and commercial aircraft. Lubricants for such applications must display an optimal thermal and oxidative stability. They are in contact with air on metal surfaces while they are hot. Therefore, from the safety standpoint, they must also have a high degree of fire resistance. In this connection their spontaneous ignition temperatures (SITs) are very important for assessing potential oil fire or explosion hazards [2,3]. Ordinarily, these values [4] are evaluated at atmospheric pressure by conventional ASTM/DIN procedures. However, as these lubricants, oils, hydraulic fluids or greases are often exposed in practice to high temperatures at elevated pressures, the corresponding SITs are needed.

Komamiya et al. [5], Davies et al. [6] and recently Raemy and Löliger [7] have shown that in principle PDSC is suitable for performing SIT determinations using a variety of materials.

The present paper demonstrates that PDSC can conveniently be used to evaluate SITs of aviation lubricants at high pressures.

### **EXPERIMENTAL**

#### *Lubricants*

Commercial pentaerythritol ester-based aviation turbine oils meeting MIL(itary) specifications: MIL-L-23699, oil A; and D.ENG.R.D. 2497, oils B, C and D [8].

Commercial hydraulic fluids: E (MIL-H-5606), hydraulic fluid, petroleum base; F (MIL-H-13919B), hydraulic fluid; G (MIL-H-17672B), lubricating oil, hydraulic system.

Commercial greases: H (MIL-G-21164), extreme pressure synthetic aircraft grease; H (MIL-G-2501), high-temperature synthetic grease; K (MIL-G-7711A), aircraft general purpose grease; L (MIL-G-81322), multipurpose grease; M (MIL-G-24139), multipurpose grease, navy.

### *PDSC standard procedure*

PDSC determinations of SITs were carried out under the following conditions: DuPont 1090 thermal analyzer with DuPont pressure differential scanning calorimeter cell; dynamic mode; heating rates variable,  $5\text{--}50^\circ\text{C min}^{-1}$ ; sample mass, 3.0 mg; sample pans, Al, Cu, Fe, open; synthetic air or oxygen with variable pressures; for further details, see text.

## RESULTS AND DISCUSSION

### *SITs of aviation turbine oils*

Figure 1 demonstrates a typical result. The spontaneous ignition temperature ( $^\circ\text{C}$ ) of oil B was determined on an aluminum surface, heating under 20 bar synthetic air at a rate of  $20^\circ\text{C min}^{-1}$ . A rapid rise in temperature from

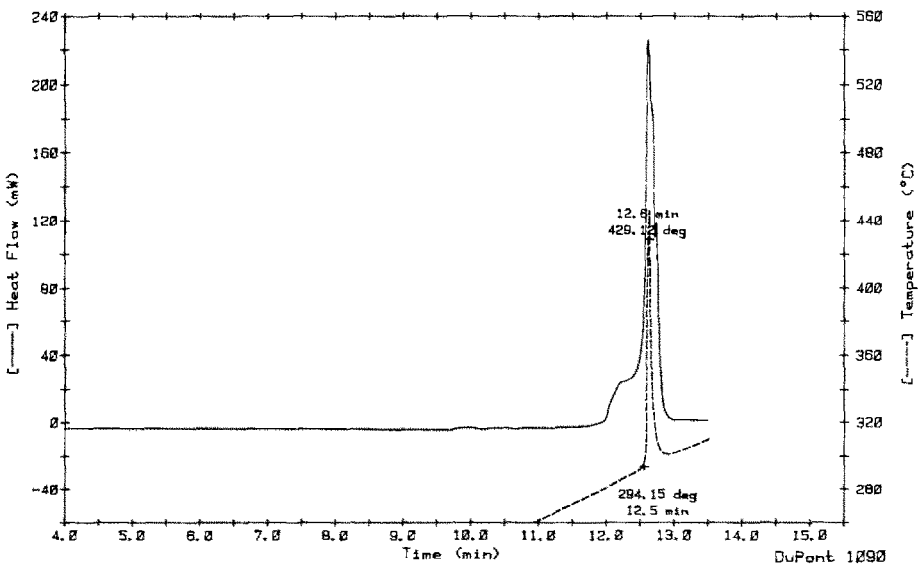


Fig. 1. Determination of the spontaneous ignition temperature (SIT) of oil B (Al sample pan; 20 bar synthetic air;  $\beta = 20^\circ\text{C min}^{-1}$ ).

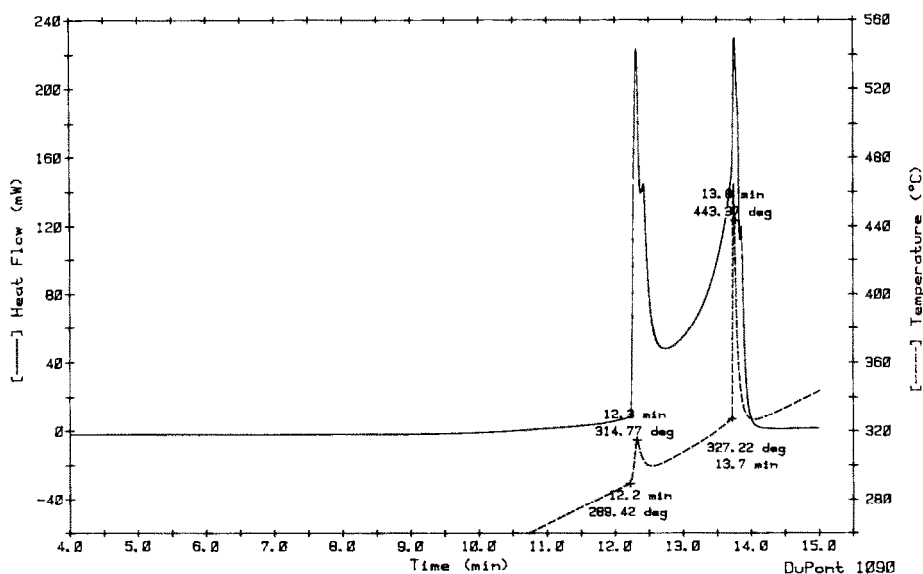


Fig. 2. PDSC diagram of oil C demonstrating incorrect ignition (Cu sample pan; 5 bar oxygen;  $\beta = 20^{\circ}\text{C min}^{-1}$ ).

294.2 to  $429.1^{\circ}\text{C}$  indicates a SIT of  $294.2^{\circ}\text{C}$ . In addition the following criteria must be met [10]: temperature rise  $\geq 100^{\circ}\text{C}$ ; explosion noise (not always detectable); rapid decrease of the heat flow to zero after ignition; empty sample pan after the test; or evenly distributed cobweblike sooty particles in the cell.

Sometimes the PDSC diagram (Fig. 2) shows two peaks for heat flow and temperature. In this case, frequently found with low heating rates or air pressure, the above criteria for spontaneous ignition were also finally reached. The second temperature rise is  $\geq 100^{\circ}\text{C}$ . Actually, the SIT of the oil is not measured at  $327^{\circ}\text{C}$ , but that corresponding to ill-defined, heavily oxidized and polymerized oil degradation residues. The increase in heat flow at  $289^{\circ}\text{C}$  is typical for the onset of the exothermic oxidative breakdown of an ester oil [11], producing a complex mixture of volatile degradation products [12].

Increasing the heating rate and/or the air/oxygen pressure easily solves the problem and gives the correct result (Fig. 1).

The results of the SIT determinations show good reproducibility. Possible runaways were eliminated according to Nalimov [9].

As a consequence of the increase in performance of modern military aero-engines, a higher temperature level of the engine particularly affects the oxidative oil degradation. In extreme cases, due to hot spots in the oil/air system and for other reasons, spontaneous ignition can occur in the bearing chamber or elsewhere, leading eventually to serious damage of the engine. For working out countermeasures it is of vital interest to know how sensitive

different brands of engine oil are corresponding to a certain military specification (e.g., oils B, C) to spontaneous ignition [2].

For this practical application, DIN/ASTM-determined SITs are usually not applicable.

Unfortunately, our first results with oils B–D and standard aluminum sample pans have shown no relevant difference in SITs ( $\beta = 20^\circ\text{C min}^{-1}$ ; 20 bar air).

Oil B  $\bar{x} = 296.8 \pm 5.0^\circ\text{C}$  ( $\pm 1.8$ ; 95%; 5)

Oil C  $\bar{x} = 297.1 \pm 2.7^\circ\text{C}$  ( $\pm 1.0$ ; 95%; 5)

Oil D  $\bar{x} = 298.1 \pm 3.1^\circ\text{C}$  ( $\pm 1.1$ ; 95%; 5)

Therefore we had to optimize the PDSC parameters to find possible SIT differences.

#### *Sample pan metals*

Table 1 shows the results using different metal surfaces. Only a copper surface is able to differentiate between SITs, oil B being the best version of the various brands, oil D the least suitable. With steel surfaces the stringent conditions for spontaneous ignition are not fully met. Temperature rise is between 80–100°C and there are black laquer-like combustion residues in the sample pan. The catalytic influence of steel is tremendous and the SIT values are the lowest observed.

#### *Heating rate, $\beta$*

Figure 3 summarizes the influence of  $\beta$  on SITs of oils B–D under 20 bar synthetic air on Cu pans. Self ignition occurs only with  $\beta \geq 10^\circ\text{C min}^{-1}$  (oils C, D) and  $\beta \geq 15^\circ\text{C min}^{-1}$  (oil B). High heating rates decrease the SIT differences between the individual oils, thus reducing the chance of differentiation.

TABLE 1

Influence of sample pan material on SITs ( $^\circ\text{C}$ ) ( $\bar{x}$  from  $N = 5$ ;  $\beta = 20^\circ\text{C min}^{-1}$ ; 20 bar synthetic air)

Metal	Oil B	Oil C	Oil D
Yellow brass	287.1	286.0	285.7
Iron	294.9	285.4	283.0
Steel <sup>a</sup>	282.1	280.8	278.8
Copper	322.0	293.7	285.4
Aluminum	296.8	297.1	298.1

<sup>a</sup> Conditions of spontaneous ignition not fully met.

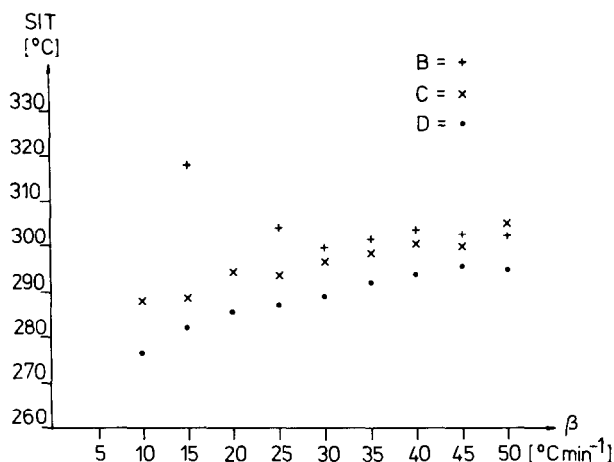


Fig. 3. Influence of the heating rate,  $\beta$  on SITs ( $^{\circ}\text{C}$ ) of oils B–D (Cu sample pans; 20 bar synthetic air).

#### *Oxidation medium and pressure*

Experiments with pure oxygen in the temperature range up to  $350^{\circ}\text{C}$  should not, for safety reasons, exceed 30 bar pressure because the constantan base of the DSC cell tends to fracture with brittleness. Table 2 summarizes our preliminary results with oils A–D.

Using pure oxygen reduces the SITs of oil B by about  $51^{\circ}\text{C}$  (mean) and  $21^{\circ}\text{C}$  for oils C and D. A higher oxygen pressure corresponds to lower SITs, but there is obviously no linear dependence. Increasing oxygen pressure from

TABLE 2

Influence of oxidation medium and pressure on SITs ( $^{\circ}\text{C}$ ) ( $\beta = 20^{\circ}\text{C min}^{-1}$ ;  $\bar{x}$  from  $N = 5$ )

Conditions	Oil A	Oil B	Oil C	Oil D
air, 20 bar, Cu	306.1	322.0	293.7	285.4
O <sub>2</sub> , 20 bar, Cu	261.1	274.4	272.4	266.0
$\Delta$	-45.0	-47.6	-21.3	-19.4
air, 30 bar, Cu	-	320.8	282.1	282.1
O <sub>2</sub> , 30 bar, Cu	-	266.5	261.3	259.6
$\Delta$	-	-54.3	-20.8	-22.5
O <sub>2</sub> , 10 bar, Cu	-	292.8	288.2	280.5
O <sub>2</sub> , 20 bar, Cu	-	274.4	272.4	266.0
O <sub>2</sub> , 30 bar, Cu	-	266.5	261.3	259.6
air, 20 bar, Cu	-	322.0	293.7	285.4
air, 30 bar, Cu	-	320.8	282.1	282.1
$\Delta$	-	-1.2	-11.6	-3.3
air, 20 bar, Al	-	296.8	297.1	298.1
air, 30 bar, Al	-	292.1	294.1	295.7
$\Delta$	-	-4.7	-3.0	-2.4

10 to 30 bar by 10 bar steps reduces the relative reduction in SITs. Increasing air pressures from 20 to 30 bar on Cu/Al surfaces lowers the SITs only by a few degrees Centigrade.

As a consequence of these preliminary results, our standard procedure for D.ENG.R.D. 2497 oils and comparable aviation turbine oils is: 3 mg, Cu, 20 bar air,  $\beta = 20^\circ\text{C min}^{-1}$ .

Virgin oils A–D can then be differentiated by the following, non-overlapping confidence intervals ( $^\circ\text{C}$ ): Oil A, 303.8–308.5; Oil B, 320.4–323.6; Oil C, 291.3–296.1; Oil D, 283.7–287.0.

### *SITs of hydraulic fluids and greases*

Hydraulic fluids for aircraft must have a very high fire resistance. With the fluids investigated, using the standard procedure described, no spontaneous ignition occurs. Experiment shows that 20 bar  $\text{O}_2$ , a heating rate of  $50^\circ\text{C min}^{-1}$  and aluminum pans were necessary to measure SITs with acceptable reproducibility. Table 3 shows some preliminary results. The inferior fluid is brand F. With  $N = 5$  there is no differentiation possible between candidates E and G. Whilst with fluid F and G there might be spontaneous ignition with 20 bar air and  $\beta = 20^\circ\text{C min}^{-1}$ , this is not the case with fluid E. In this case we observe self-ignition only under 20 bar pure oxygen.

With aero-greases H–M a modified procedure is also needed: Al sample pan, 20 bar  $\text{O}_2$  and  $\beta = 20^\circ\text{C min}^{-1}$ . Table 3 summarizes the SITs measured.

The inferior grease is M with a SIT of  $217.4^\circ\text{C}$ . The best candidate is obviously I which has no tendency to spontaneous ignition under the conditions employed.

TABLE 3

SITs of aero hydraulic fluids and greases ( $\bar{x}$  from  $N = 5$ )

<i>Fluids</i>	
E	$244.8 \pm 4.2^\circ\text{C}$ ( $\pm 1.5$ ; 95%; 5)
F	$232.8 \pm 2.8^\circ\text{C}$ ( $\pm 1.0$ ; 95%; 5)
G	$243.2 \pm 1.6^\circ\text{C}$ ( $\pm 0.6$ ; 95%; 5)
<i>Greases</i>	
H	$257.3 \pm 6.7^\circ\text{C}$ ( $\pm 2.4$ ; 95%; 5)
I	No ignition
K	$254.2 \pm 4.3^\circ\text{C}$ ( $\pm 1.6$ ; 95%; 5)
L	$255.3 \pm 3.5^\circ\text{C}$ ( $\pm 1.3$ ; 95%; 5)
M	$217.4 \pm 3.5^\circ\text{C}$ ( $\pm 1.3$ ; 95%; 5)

## CONCLUSION

The particular advantages we found in measuring SITs with PDSC is that the method is fast, convenient and shows good reproducibility. SIT dependence on elevated pressure, oxidation medium, catalytic activity of various metal surfaces, influence of lubricant degradation products and/or wear metals can easily be studied.

## ACKNOWLEDGMENTS

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