

SPONTANEOUS IGNITION TEMPERATURES OF AVIATION TURBINE OILS

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(Received 10 July 1986)

ABSTRACT

The usefulness of pressure differential scanning calorimetry (PDSC) in studying spontaneous ignition of aviation turbine oils is shown. The following applications are discussed: (1) determination of spontaneous ignition temperatures (SITs) of commercial aviation turbine oils; (2) catalysis of spontaneous ignition by metal/metal oxides; (3) influence of oil degradation products, like carbonaceous deposits, volatiles and wear debris; (4) inhibition by antioxidants.

INTRODUCTION

Recently Zeman et al. [1,2] reported on the usefulness of pressure differential scanning calorimetry (PDSC) in studying thermal-oxidative degradation of lubricants [1] and spontaneous ignition temperatures (SITs) of aviation lubricants [2]. Especially synthetic aviation turbine oils for modern military aircraft must have a high degree of resistance to spontaneous ignition. As a consequence of the performance increase of these aero-engines, a higher temperature level of the engine is responsible for high oxidative oil degradation. Spontaneous ignition can occur in extreme cases, due to hot spots in the oil/air system and for other reasons in bearing chambers or elsewhere, leading eventually to serious damage of the engine [3]. It is therefore of vital interest to know the spontaneous ignition temperatures (SITs) of selected brands of turbine oils. For this particular problem SITs determined by conventional techniques are usually not applicable, because as these oils are exposed in practice to high temperatures at elevated pressures, the corresponding values are needed. In addition, information is required on: catalytic activity of selected metal/metal oxides and wear metals; influence of lubricant degradation products, like deposits and volatiles; dependence on the ageing state, e.g., on remaining antioxidant concentrations.

In this paper we report our first results which show that PDSC can conveniently be used to evaluate parameters influencing SITs of aviation turbine oils.

EXPERIMENTAL

PDSC standard procedure

PDSC determinations were carried out under the following conditions: Du Pont 1090 Thermal Analyzer with Du Pont pressure differential scanning calorimeter cell; dynamic mode; heating rate $20^{\circ}\text{C min}^{-1}$; sample mass 3.0 mg; aluminum sample pans; synthetic air 20 bar pressure; for further details ref. 2. SITs from $N = 5$; 95% confidence interval.

Aviation turbine oils

Commercial oils used are as described in the text. Metal/metal oxide catalysis and solid oil degradation products were 1.5 mg of powdered material added to 3.0 mg of O-160 Oil A₁ in an aluminum sample pan.

Model oils used were pentaerythritol base oil Hercolube J and 0.5–5 mass% amine antioxidants. For details see Figs. 4 and 5 and text.

RESULTS AND DISCUSSION

SITs of commercial aviation turbine oils

Figure 1 shows some typical results for different brands of engine oil corresponding to certain military (MIL) specifications; D.ENG.R.D. 2497/O(il)-160, MIL-L-23699/O-156, MIL-L-7808-F/O-148 and D.ENG.R.D. 2487/O-149.

Oils O-160/O-156 are pentaerythritol ester-based fluids containing the antioxidant combinations *p*, *p'*-di-tert-octyldiphenylamine (DODPA)/phenothiazine (PTZ) or DODPA/phenyl-1-naphthylamine (PAN), resp. DODPA/*p*-tert-octyl-phenyl-1-naphthylamine (OPAN). Oils O-148/O-149 are mostly diester-based lubricants inhibited with the antioxidants mentioned and in the case of O-149 fluids containing thickener (viscosity 7.5 cSt/210°F). There is no extreme difference between the various brands of O-160/O-156 oils, as shown in Fig. 1. Mean values are 302°C resp. 300°C as determined with the standard procedure (20 bar air/ $\beta = 20^{\circ}\text{C min}^{-1}$). These results of a static test compare well with values in the region of $310\text{--}320^{\circ}\text{C}$ obtained by a dynamic test/mtu-rig test, which was carried out to simulate real engine conditions by varying air flow ratios, thickness of oil films, residence time and ratio of oil/air mixture [3]. The lowest SITs of 160-oils at 280°C (1 bar) are obtained by a static pressure method/BAM-bomb test, using a stoichiometric oil/air mixture [3,4].

Results of conventional DIN/ASTM static tests at atmospheric pressure show considerably higher values, e.g., $400 \pm 5^{\circ}\text{C}$ [4]. Therefore, these tests

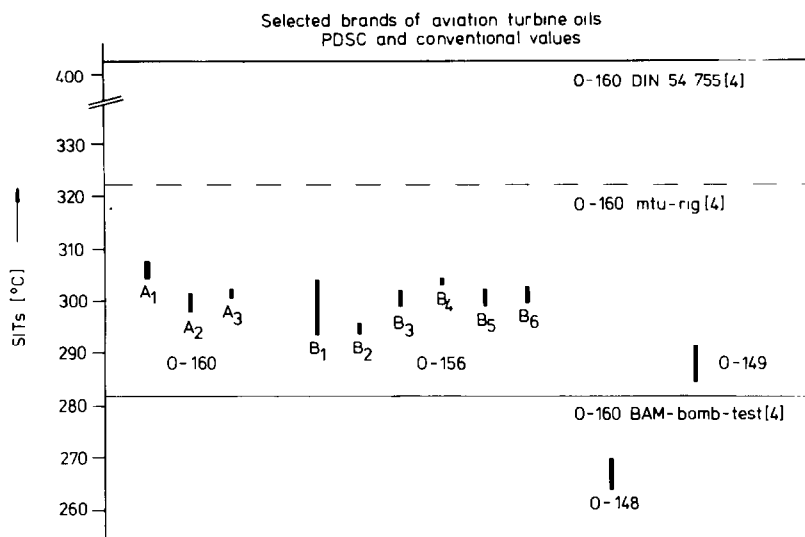


Fig. 1. Typical SITs for different brands of engine oils.

are considered inapplicable for this practical application. The advantage of the PDSC-method as compared to the mtu-rig test and the BAM-test is, that it is faster, convenient and shows good reproducibility while its results are practice oriented.

Diester-based fluids have considerably lower SITs as shown in Fig. 1. This is in accordance with the known thermal instability of the diester molecule. From a more practical point of view, it is of interest that by selecting base fluid/antioxidant combinations, optimal stabilization against spontaneous ignition is possible, e.g., oil A₁ in Fig. 1.

Catalysis of spontaneous ignition by metals / metal oxides

Metals/metal oxides present in turbine bearings exert a catalytic influence on antioxidant depletion and thermal-oxidative oil degradation in service and, therefore, SITs are also influenced by catalysis [5,6].

In a previous publication [1] it was shown that catalytic effects can be investigated by using PDSC and sample pans made of the metals in question. In order to investigate also the catalytic influence of metal oxides, it is more convenient to work with an addition technique. For the measurement of SITs under the conditions in the bearing chamber, the oil samples are mixed with powders of metal/metal oxides in an aluminum pan. This simulates the coexistence of oil with iron rust, wear particles or porous carbonaceous deposits found in the oil/air system. Figure 2 shows the results on SITs influenced by the presence of certain metal/metal oxides. The virgin oil was used as a reference.

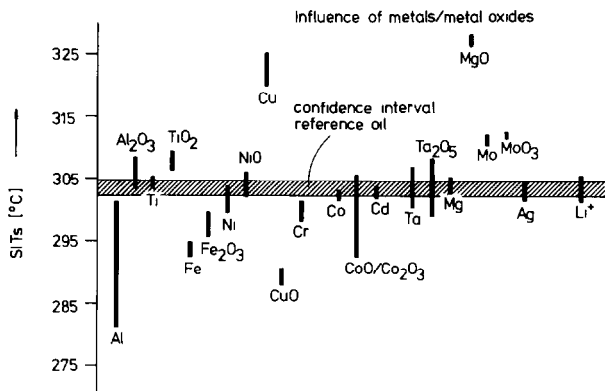


Fig. 2. Influence of metal/metal oxides on the SIT of O-160 oil A₁.

Pure aluminum powder shows a distinct reduction of the SIT of the reference oil but the confidence interval is exceptionally wide. As expected, aluminum oxide is not active. Titanium is without influence, but TiO₂ increases the SIT from 303.5 to 307.9°C. As known from previous measurements of the catalytic influence of iron/iron oxides on the thermal-oxidative stability of aero engine oils [1], they are highly reactive and significantly decrease SITs. Pure nickel has a slight tendency to decrease SITs as shown in Fig. 2, while NiO is inactive. The preliminary data on Cu/CuO are ambiguous. Addition of copper powder to the oil increased SITs from 303.5 to 323°C, but a detailed interpretation of the heat flow curve shows that the oil sample is heavily oxidizing before spontaneous ignition occurs. Therefore, it might be possible that in this case the SIT of an ill-defined oxidized and polymerized oil was actually measured. As expected, CuO is the catalytically most active compound studied.

Co is not active, nor are Cd, Ta, Ta₂O₅, Mg or Ag. Cobalt(II)/(III)-oxides induce a slight decrease of the SITs, as does metallic chromium.

The high value in the presence of MgO was quite unexpected, this oxide seeming to be a good inhibitor of spontaneous oil ignition. A possible explanation is that basic MgO decomposes peroxides and acid precursors during thermal-oxidative oil breakdown, as is the case with sodium hydroxide [7]. Thus, MgO obviously reduces the formation of volatile degradation products responsible for a low ignition temperature.

Molybdenum and its oxide also have a distinct stabilizing effect as shown in Fig. 2, in agreement with results on its ability to influence the oil-ageing process [1].

Earlier work on the effect of alkali metal ions on thermal oxidative oil stability [8] could be confirmed in our laboratory by Steinwasser [9] using PDSC. Therefore, it was of interest to investigate whether SITs could possibly be influenced. Our measurements with lithium perfluorobutyrate (0.2–0.5 mass%) show that this is not the case.

Influence of oil degradation products on SITs

When operating at high temperatures in the presence of oxygen and catalytically acting metals, the oils are severely stressed. These conditions may lead to rapid antioxidant depletion and subsequent oxidative degradation of the ester base. By peroxide formation and degradation, volatile products, such as acids, esters, ketones, aldehydes and lactones, are produced [10,11]. In a further step, high molecular weight, but still partially oil soluble compounds, are formed [12]. These are intermediates in the formation of insoluble sludge and finally in solid carbonaceous deposits. The effects of deposits include [13]: obstruction of heat exchange, corrosion problems, damage of bearings and gears, and clogging of filters. They should also be considered potentially dangerous of causing spontaneous ignition, until studied further.

Figure 3 summarizes our first results on carbonaceous deposits and simuli. Carbon particles from previous spontaneous ignition experiments were collected and added to an O-160 oil. SIT determination shows no significant deviation from the SIT of the virgin oil. With activated carbon there is a distinct decrease, but this result might be influenced by surface effects. The investigation of solid deposits from real engines (samples S_1 – S_3 provided by Dr. K. Maier, Motoren- und Turbinen-union, Munich, West Germany) was most interesting. The samples are taken from different parts of the oil/air system, having different C/H/N ratios and metal contents (see Table 1).

The samples were powdered and added to an O-160 oil. Only the S_2 deposit shows a decrease of the SIT, S_1 and S_3 are without effect (overlapping confidence intervals). Clearly, much more work in this field is necessary for a final conclusion. Spontaneous ignition of oil-free samples S_2 and S_3 was not possible under standard conditions, only oxidative degradation. Since solid deposits from real engines are always contaminated with wear

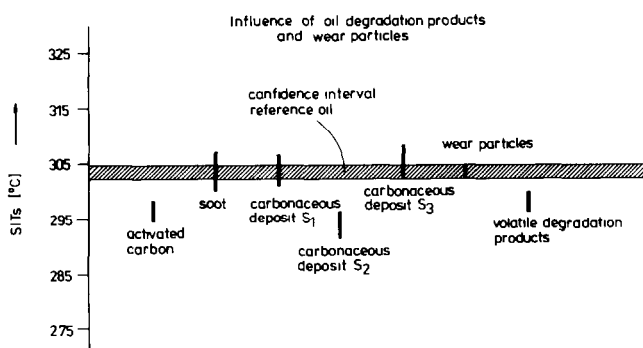


Fig. 3. Influence of oil degradation products and wear debris on the SIT of O-160 oil A_1 .

TABLE 1

Sample	C	H	N	% total metal ^a content	% Fe
S ₁	60.13	3.91	1.20	4-5	2.6
S ₂	70.48	7.23	3.63	2-3	0.8
S ₃	41.81	5.32	2.35	4-5	2.7

^a Selected bearing metals only: Fe, Ni, Cr, Co, Cu, Al, Mg, Ag, Zn, Cd, Pb.

metals, typical wear particles, isolated from used oil by filtration ($\geq 25 \mu$), were included in the above experiments. Analysis shows Ni, as well as Al, Fe, Mn, Ca and Si [14]. Despite this composition, the added wear particles did not decrease the SIT of the virgin oil.

To investigate the influence of volatile oil degradation products, we added 10 mass% of a typical mixture, containing esters, acids, ketones, aldehydes and lactones [10,11] to the reference oil. The result shows a distinct decrease of the SIT from 303.5 to 298°C (Fig. 3). In earlier measurements using Cu-sample pans we observed a reduction of up to 20°C upon addition of volatile degradation products [15]. These results are especially important in relation to occurrence and prevention of oil fire in a real aero engine.

Inhibition of spontaneous ignition by antioxidants

Temperatures in the engine oil system will increase even higher in the future, thus increasing the danger of spontaneous oil ignition. Therefore, the paramount problem for the oil chemist is to stabilize oils and decrease their tendency to ignite, by using additives. Ignition always occurs in the gas phase. With aviation turbine oils this is a mixture of oil vapor and volatile degradation products in variable stoichiometric composition.

Reducing oil volatility and inhibition of thermal-oxidative breakdown of the oil, should obviously result in higher SITs. Results with a pentaerythritol ester base oil containing variable amounts of *p*, *p'*-di-tert-octyldiphenylamine (DODPA), *p*-tert-octyl-phenyl-1-naphthylamine (OPAN), resp. phenothiazine (PTZ) show that this is the case. In order to simulate two commercial aviation turbine oils of the O-160 type, we also investigated antioxidant combinations, e.g., DODPA/OPAN and DODPA/PTZ in a total concentration range of 0.5–5 mass%. These experiments were especially designed to detect possible synergistic effects. Our results are presented in 3D-plots (Figs. 4 and 5). Based on the PDSC results, the following statements are possible:

(i) The order of effectiveness of pure antioxidants is PTZ > OPAN > DODPA.

(ii) Increasing the antioxidant concentration increases SITs.

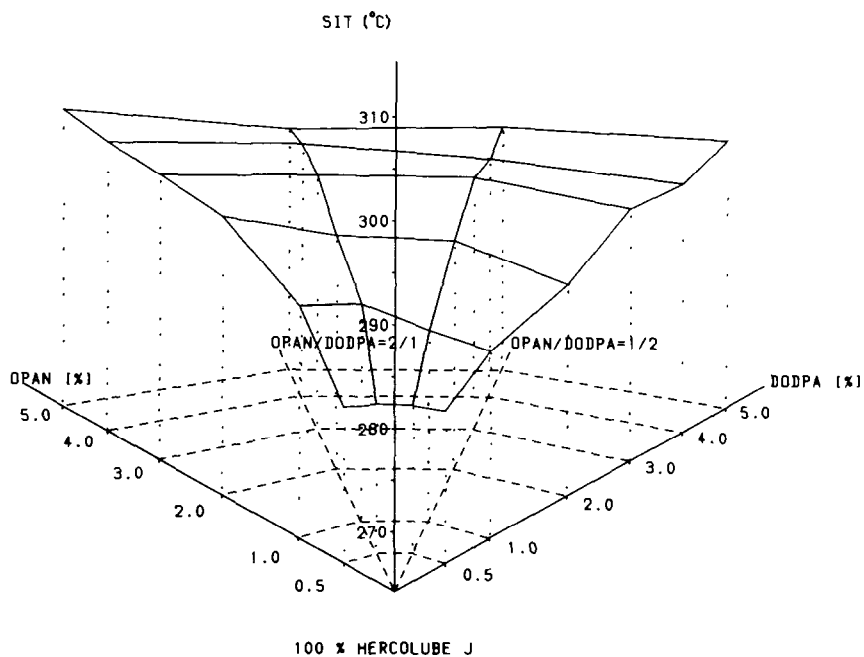


Fig. 4. SITs of model oils based on a pentaerythritol ester (Hercolube J) and antioxidants DODPA/OPAN/3D-plot.

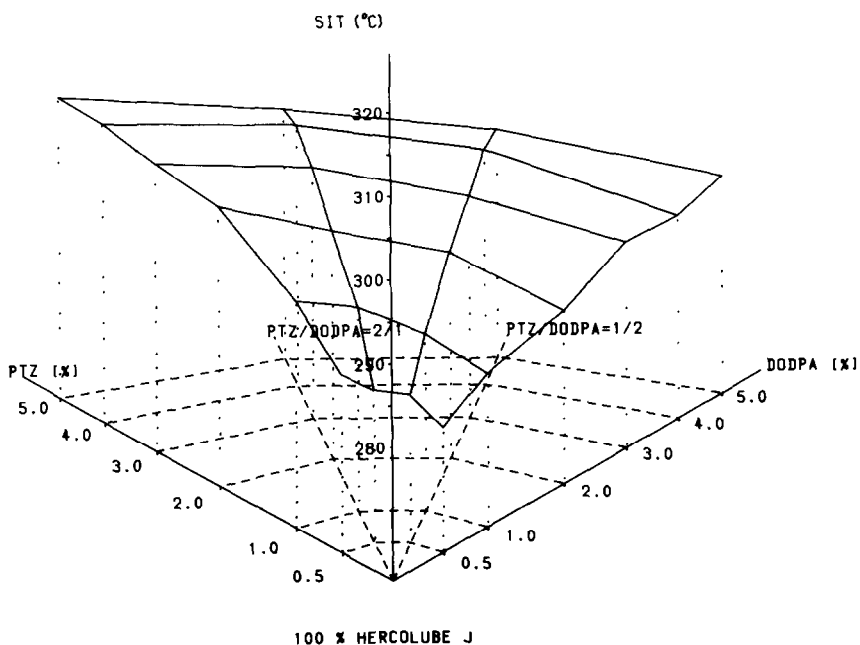


Fig. 5. SITs of model oils based on a pentaerythritol ester (Hercolube J) and antioxidants DODPA/PTZ/3D-plot.

(iii) No synergistic effects between DODPA/OPAN and DODPA/PTZ combinations could be detected.

This shows that by inhibiting thermal-oxidative oil degradation, spontaneity of oil ignition is significantly reduced. This opens new possibilities to the experienced oil/additive chemist for oil fire inhibition.

CONCLUSIONS

Our investigation demonstrates that parameters influencing spontaneous ignition of aviation turbine oils can be studied conveniently by PDSC. SITs of selected ester oils determined by PDSC compare well with values from dynamic and static tests which are used to simulate real engine conditions. Preliminary results on catalysis by metal/metal oxides, show that metallic iron, iron oxide and cupric oxide considerably lower the susceptibility to spontaneous ignition, while magnesium oxide has a pronounced stabilizing effect. Carbonaceous deposits and volatile oil degradation products can also lower SITs. Selected amine antioxidants effectively inhibit spontaneous ignition of ester oils. Therefore it should be possible, with modern additive technology, to solve the problem of oil fires.

ACKNOWLEDGEMENTS

A research grant by the West German Ministry of Defence (BMVg/Rü III.7) is gratefully acknowledged. We thank W. Duester for providing 3D-plots and Dr. K. Maier of Motoren- und Turbinen-union, Munich, West Germany, for samples of carbonaceous deposits and wear debris from engines.

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