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Deposit formation in aero engines — investigation by pressure differential scanning calorimetry (PDSC)

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Abstract

Pressure differential scanning calorimetry has been used to evaluate the deposit-forming tendencies of selected aero engine oils. In order to simulate real aero engine conditions, oil oxidation was carried out in thin films under 8 bar of air pressure. The factors affecting deposit formation are discussed.

The method is a rapid and effective technique for screening the deposit-forming tendencies of aero engine oils and similar lubricants or other fluids under a variety of conditions.

INTRODUCTION

Thermal-oxidative stability is one of the most important parameters for achieving the maximum service life of aero engine oils by minimizing in-service engine problems such as viscosity increase, corrosion, and polymeric deposit formation.

Both the rate and degree of lubricant degradation occurring in an aero engine depend upon lubricant aeration, lubricant temperature and contact with catalytically active metal surfaces. For aero engines operating under normal conditions, the rate of degradation is usually low, but changes in engine operating conditions resulting, for example, in higher oil temperatures, may lead to rapid antioxidant depletion and subsequent oxidative degradation of the ester base [1, 2]. This is the case in most modern military aircraft with increased performance, long-term oil temperatures of around 150°C and peak temperatures of between 300 and 400°C. Oil ageing produces volatile aldehydes, ketones, acids, esters and lactones. Oligomers/polymers are formed which increase oil viscosity and eventually lead to oil-insoluble sludge and deposits, causing a potential danger for the oil–air system of the engine [3–6]. Thin oil films and hot spots in the oil–air system of an aero engine are mainly responsible for deposit formation. Polymeric

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deposits may block oil jets and breather lines, clog filters and obstruct heat exchange.

For the investigation of the deposit-formation tendency of aero engine oils, there are several more or less practicable methods available. These include bearing deposition tests [7–9], a tube deposition test [10], a hot-wall deposition test [11], a rotating cylinder deposition test [12], an engine simulator test [13] and the Mobil spinning disk test [14]. Because test parameters are quite varied, correlation between several methods and with actual aero engine performance is limited.

Most of the bearing tests [7–9] require large oil samples, and are time-consuming and expensive. Newer approaches include the modified panel coker and the modified static deposition tester [15, 16], especially a small test-volume, low-cost version [17], and the Penn State micro-oxidation test [18].

Recently, Zeman [19, 20] reported on the usefulness of pressure differential scanning calorimetry (PDSC) in studying the thermal-oxidative degradation of lubricants and related problems including lubricant deposition phenomena.

In this paper we report some preliminary results on the deposit-forming tendencies of aero engine oils. In the course of our work, a similar method based on PDSC was published by Zhang et al. [21] to evaluate Diesel engine piston deposit formation.

EXPERIMENTAL

Lubricants

Commercial aero engine oils based on pentaerythritol ester and trimethylolpropane ester, meeting MIL(itary) specifications MIL-L-23699 and DERD 2497 and containing different antioxidant packages, were used. The base ester fluid was Hercolube J.

PDSC standard procedure

A Du Pont 1090 thermal analyzer was used with a Du Pont pressure differential scanning calorimeter cell; the isothermal mode constant was 120 min at 240, 250, 260, and 270°C for producing deposits; 8 bar of air at a flow rate of 50 ml min^{-1} were employed with 3.5 ± 0.1 mg oil samples. The sample pans were of aluminum (Du Pont) and X10CrNiTi89 steel (home made). The combustion of the deposit formed took place in O_2, using dynamic mode, $\beta = 20°C\ min^{-1}$ from isothermal to 400°C (450°C).

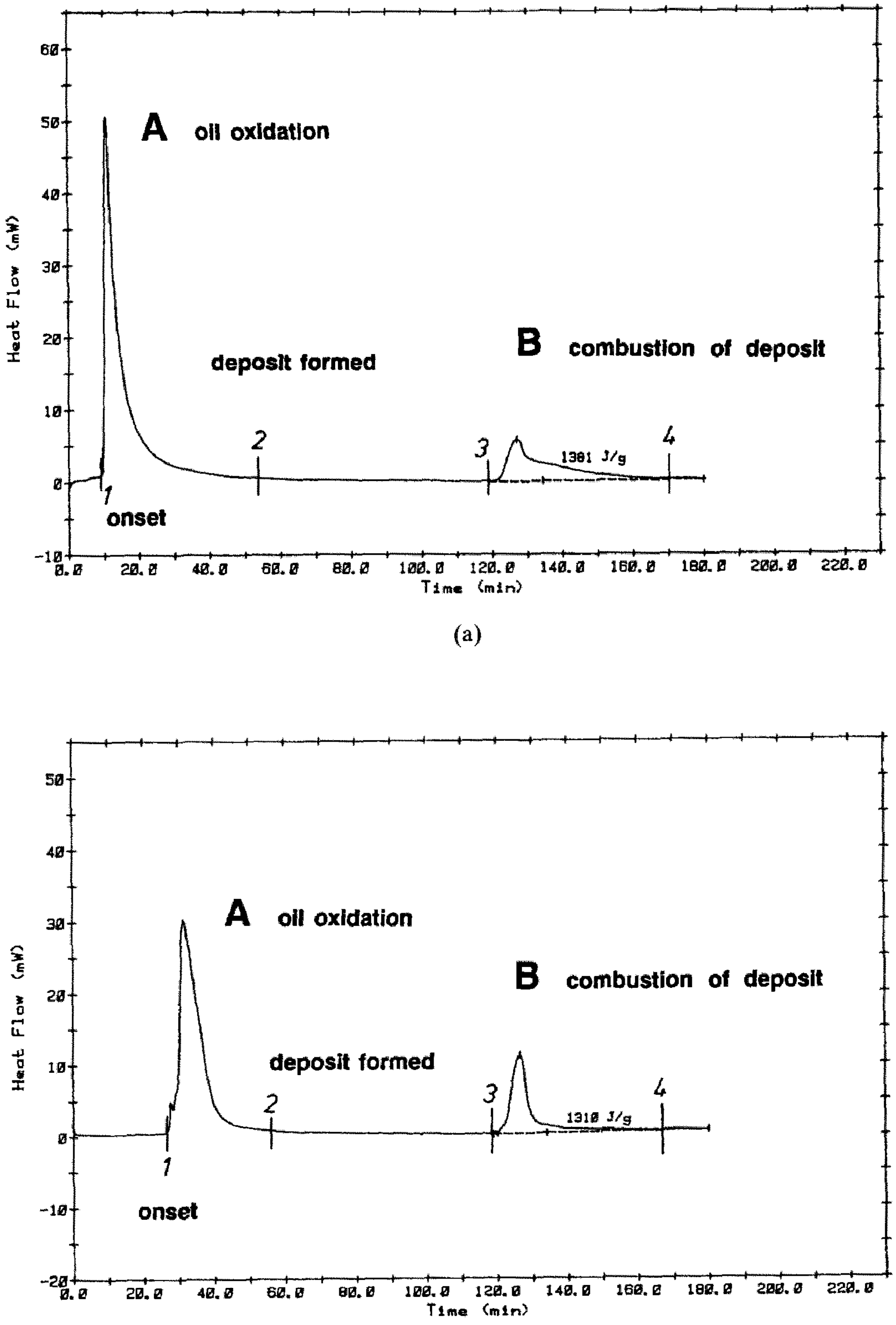
RESULTS AND DISCUSSION

Figure 1 shows typical results of oil oxidation at 250°C (peak A) and subsequent combustion of the deposit formed (peak B) on a steel (a) and aluminum (b) surface. To determine the deposit-forming tendency of an oil, the thermal oxidative ageing was carried out in the DSC cell under exactly defined, variable conditions of time and/or temperature in thin films with unlimited access of oxygen (5–10 bar air pressure, open sample pan).

Peak A represents oil oxidation and is mainly used to determine the isothermal onset time of oxidation, **1** [19]. The exothermic chemical reactions occurring are formation of volatile ageing products and fast polymerization/polycondensation of the active deposit precursors present. In the case of pentaerythritol-based ester oils, we were recently able to identify the principal polymer structures in the primary ageing state as dicarboxylic acid polyesters and some very complex polar ester structures [6]. After oxidation of the oil, e.g. about 40 min at 250°C on steel, Fig. 1(a), **2**, the sample pan contains a dark brown, lacquer–like, sometimes brittle solid deposit as can be seen by opening the DSC cell. Because a direct deposit mass determination is impracticable, the deposit was burnt up by automatically changing the DSC cell atmosphere to pure oxygen using a dynamic temperature rise (see the Experimental section, above). The resulting combustion enthalpy (peak B) was measured, e.g. 1381 J per g oil, Fig. 1(a).

If the mean combustion enthalpy of deposits based on various ester oils and formed under real aero engine conditions, or in simulated deposit tests, is known, calculation of the absolute amount of deposit (g per g of oil) seems possible. Because deposit formation in the DSC cell depends on many experimental factors, e.g. isothermal test temperature, sample pan metal surface, amount of oil, air flow rate, and pressure and time at test temperature until deposit combustion, **2**–**3**, it is necessary to define standard test conditions [22, 23] (see the Experimental section). Standardization allows investigation within an acceptable period of time of the reaction temperatures, the catalytically active metals, the antioxidant package, the ageing state of the oil, and the oligomeric deposit precursors and the amount of deposit formed.

It is very important to note that different oils may have different evaporation characteristics with respect to oil and volatile oil oxidation products. Those oils that volatilize easily may lose a significant fraction of the sample before oxidation and polymerization/polycondensation reactions are complete, and may, therefore, produce only a small amount of deposit. We use synthetic air pressures of 5–10 bar to suppress oil volatilization but mainly for reasons of simulating oil performance in a real aero engine environment. Therefore only oils of very similar evaporation characteristics can be evaluated with respect to the deposit-forming factors



(a)

(b)

Fig. 1. Typical results of oil oxidation at 250°C (peak A) and subsequent combustion of the deposit formed (peak B) on a steel (a, above) and aluminum (b, below) surfaces.

mentioned above. Oil volatilization under the employed DSC test conditions should be examined by thermogravimetry (TG) if not yet known.

Repeatability of combustion enthalpy measurements

Table 1 shows that the combustion enthalpies determined under standard conditions for MIL-L-23699 oil D on aluminum and X10CrNiTi89 steel surfaces are sufficiently repeatable.

TABLE 1

Repeatability of combustion enthalpy measurements [22–25] at 250°C, MIL-L-23699 oil D, standard conditions, on X10CrNiTi89 steel and aluminum surfaces

Experiment	Enthalpy (J g^{-1} oil)	
	Steel surface	Aluminum surface
1	1289	1212
2	1413	1357
3	1504	1310
4	1580	1319
5	1595	1202
6	1381	1215
7	1456	1251
8	1446	1176
9	1402	1164
10	1413	1087
Mean value [a]	1448 ± 92	1229 ± 82
Standard deviation (rel. %)	±6, 3	±6, 6

[a] Free of runaways [26].

Therefore the mean value in subsequent experiments was calculated from $N = 5$ determinations, free of runaways according to the Nalimov test [26]. The repeatability of the determinations using aero engine oils of different compositions might be influenced by the antioxidant package present, especially on steel surfaces.

Mean combustion enthalpy of laboratory-produced deposits and deposits formed from aero engines

Laboratory deposits were produced from various pentaerythritol-ester-based and trimethylolpropane-ester-based aero engine oils and base fluids (Hercolube J, pentaerythritol tetraheptanoate and pentaerythritol tetranonanoate) [27]. Deposit samples from real aero engines (gear box, compound shaft and bearing) were provided by Dr. K. Maier, MTU

TABLE 2

Determination of a mean combustion enthalpy of laboratory-produced deposits and aero engine deposits [23] at 250°C, modified standard condition on aluminum surface

Deposit from	Deposit no.	Enthalpy ($J g^{-1}$ deposit)
Laboratory bench test, $N = 2$	1	8593
	2	8956
	3	8649
	4	8820
	5	9760
	6	9552
	7	8080
Real aero engines, $N = 1$	1	7094
	2	8312
	3	9457
Mean value		8727 ± 790 [a]
Standard deviation (rel. %)		±9

[a] Preliminary value, depending on experimental conditions, e.g. hold time **2**→**3**.

Motoren- und Turbinenunion, Deutsche Aerospace, Munich. Combustion enthalpy measurements, shown in Table 2, give a mean value of 8727 J per g of deposit as determined under standard conditions (see the Experimental section). This value was used to estimate the absolute amount of deposit formed per g of oil applied.

Deposit-forming tendencies of selected aero engine oils

Table 3 summarizes some of our preliminary findings on the deposit-forming tendencies of aero engine oils. As expected, there are significant differences both on steel and aluminum (Al_2O_3) surfaces. The use of phenothiazine(s) in the antioxidant package, in particular, significantly increases the amount of deposit, as was also shown in investigations with Hercolube-J-based simulated oils (Table 4). Table 4 demonstrates that under the conditions employed, the antioxidant structure and its concentration are important factors. The quantity of deposit formed seems to decrease and then increase as the antioxidant concentration is further increased for DODPA and OPAN antioxidants.

Table 5 shows the influence of the isothermal reaction temperature on deposit formation. Increasing the reaction temperature obviously reduces the amount of deposit formed by increasing the ratio of volatilization to polymerization and polycondensation. The importance of the oil volatilization characteristics has already been mentioned. The hold time at reaction temperature also affects the amount of deposit as shown in Table 6 (see Fig.

TABLE 3

Deposit-forming tendencies of selected MIL-L-23699 and DERD 2497 oils and one ester-based oil under thin film conditions [23–25] at 250°C, standard conditions, on X10CrNiTi89 steel and aluminum surfaces

Oil [a]	Gram deposit per g oil ($N = 5$)	
	Steel	Aluminum
Spec. MIL-L-23699/NATO Code 0-156		
A_1	0.090 ± 0.005	0.081 ± 0.010
A_2	0.132 ± 0.011	0.085 ± 0.005
D_1	0.166 ± 0.010	0.141 ± 0.006
D_2	0.121 ± 0.007	0.079 ± 0.006
Spec. DERD 2497/NATO Code 0-160		
D	0.166 ± 0.010	0.141 ± 0.006
BII	0.119 ± 0.003	0.089 ± 0.005
C	0.176 ± 0.007	0.155 ± 0.007
Hercolube J	0.191 ± 0.013	0.126 ± 0.009
Standard deviation (rel. %)		±6–8

[a] Key: see our earlier publications [1, 2, 5, 19].

1a, time **2–3**, about 80 min). The deposit already formed (point **2**) reacts further by slow oxidation and/or pyrolysis producing volatiles until combustion (point **3**). Because the reaction rates might differ it is advisable to keep the hold time constant. Variation of the hold time, however, allows investigation of deposit stability.

Earlier work [23] has shown that the PDSC method is also applicable to

TABLE 4

Influence of antioxidant structure and concentration on the deposit-forming tendencies of simulated aero engine oils [23]; antioxidants: *pp'*-dioctyldiphenylamine (DODPA), *p*-octylphenyl-1-naphthylamine (OPAN), phenothiazine (PTZ) in Hercolube J; at 250°C, modified standard conditions, aluminum surface

Oil	Deposit-forming tendency [a]		
	DODPA	OPAN	PTZ
Uninhibited	1	1	1
1 mass %	0.9	1.0	1.4
2 mass %	0.9	0.9	1.9
3 mass %	1.2	1.1	1.8

[a] Data normalized to base oil = 1.

TABLE 5

Influence of reaction temperatures on the deposit-forming tendencies of selected aero engine oils [23] using modified standard conditions and aluminum surface

Reaction temperature (°C)	Oil designation [a]		
	BII	C	D
240	1	1	1
250	0.74	0.96	0.91
260	0.66	0.86	0.86
270	0.56	0.63	0.67
280	0.55	0.60	0.47

[a] Data normalized to amount of deposit at 240°C = 1.

TABLE 6

Thermal-oxidative stabilities of deposits using modified standard conditions, 250°C, aluminium surface

Hold time (min) at 250°C	Oil designation [a]	
	BII	D
0	1	1
15	0.93	0.91
25	0.90	0.92
110	0.64	0.74

[a] Data normalized to zero hold time = 1.

the examination of other lubricants, e.g. di-ester oils, poly-α-olefines and mineral oils.

CONCLUSIONS

The deposit-simulation test method developed is a rapid and effective technique for screening the deposit-forming tendencies of aero engine oils and similar fluids. The method needs only very small amounts of oil and the results are of sufficient repeatability. Important influences, for example the action of temperature, metal surface, antioxidant package, possible active deposit precursors and the ageing state of the oils, can be determined within an acceptable period of time.

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