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THE DSC CELL—A VERSATILE TOOL TO STUDY THERMAL-OXIDATIVE DEGRADATION OF LUBRICANTS AND RELATED PROBLEMS

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ABSTRACT

The versatility of a differential scanning calorimetry (DSC) cell in studying thermal and/or thermal-oxidative degradation of lubricants is shown using ester based aviation turbine oils as an example.

The following applications are discussed:

(1) quality control of used oils by pressure differential scanning calorimetry (PDSC);

(2) influence of metal catalysis on oil degradation;

(3) identification of volatile degradation products by PDSC–gas chromatography (GC)–mass spectrometry (MS) via a TENAX GC trap.

INTRODUCTION

We are interested in the thermal-oxidative stability of ester based lubricants. Organic esters represent one of the largest volume synthetic lubricants in use today. The principal use of these fluids is still in the lubrication of jet engines for military and commercial aircraft. Two classes of esters are defined by Military Specifications MIL-L-7808 and MIL-L-23699. Dibasic esters are used in the formulation of MIL-L-7808 lubricants, and esters of neopentylpolyols, such as pentaerythritol and/or trimethylolpropane with fatty acids C_5–C_{10}, are used to meet specifications MIL-L-23699 or D.ENG. R.D. 2497. Thermal-oxidative stability is one of the most important parameters responsible for the maximum service life of aviation turbine oils. Both rate and degree of lubricant degradation occurring in a turbine engine depend upon lubricant aeration, lubricant temperature and contact with catalytic active metal surfaces. For normal operating engines, the rate of degradation is usually low, but changes in engine operating conditions, e.g., increased availability of oxygen and higher temperatures, may lead to rapid antioxidant depletion and subsequent oxidative degradation of the ester base. In addition to the need for a method identifying abnormally working engines which cause high rates of lubricant breakdown, fast and efficient

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methods are needed to determine the thermal-oxidative stability of new oil formulations and the remaining stability of used oils for establishing optimal oil drain periods.

Thermal analytical methods, like DTA and DSC, allow a fast and reliable determination of the thermal and/or thermal oxidative stability [1–11].

We have investigated extensively the thermal-oxidative stability of synthetic ester oils by DSC [11]. In order to avoid problems with the high rate of evaporation of the lubricants, it is advisable to use PDSC. The results have shown also that dynamic PDSC is not the optimal method for determining the quality of new oils of similar composition or used oils, because the difference in onset temperatures is often very small. In contrast, isothermal PDSC is extremely useful for this purpose [11]. Recently, we have shown that quality control of used aviation turbine oils can be done very efficiently by high performance liquid chromatography (HPLC)/PDSC determinations [12,13]. The intention of this paper is to show that the DSC cell is a very versatile tool for studying lubricant degradation. In addition to pure calorimetric measurements, the influence of metal catalysis can be studied, and the identification of volatile degradation products is also possible by combining the cell with gas chromatography–mass spectrometry (GC–MS) using a TENAX trap.

EXPERIMENTAL

Oils

Commercial pentaerythritol ester based aviation turbine oils inhibited with *p,p′*-dioctyldiphenylamine (DODPA)/phenothiazine (Phtz), oil A, and DODPA/octylphenyl-1-naphthylamine (OPAN), oil B.

PDSC standard procedure

PDSC was carried out under the following conditions.

DuPont 1090 Thermal Analyzer with DuPont pressure-differential-scanning-calorimeter cell; isothermal mode; measuring temperatures, T_M, 220–280°C; sample mass 3.0 mg; standard sample pan Al, open; synthetic air with 5 bar pressure; for details see ref. 11. $\bar{x}$ was calculated from five determinations statistically pure according to Nalimov [14]; correlation of ln $\bar{x}$ with T^{-1} by linear regression.

Metal catalysis

Other sample pans are commercially available, Cu, Au (DuPont), steel (Perkin-Elmer) or homemade from commercial metal foils (Koch Light

Laboratories Ltd.): Ni (99.7%, No. 8505-00); Mo (99.9%, No. 8476 h); Zn (99.9998%, No. 66249); Ti (99.9%, No. 8754-00); Cd (99.9999%, No. 8108 h); Ta (99%, No. 8754-00); Iron St 14; Cr/Ni steel.

Isolation of volatiles on TENAX GC

A TENAX GC trap was connected to the exit port of the DuPont DSC cell. The trap, a glass injection port liner (Carlo Erba Fractovap 2900; 6 mm OD, 2 mm ID, contained 30 mg TENAX GC (60–80 mesh). Gas sample volumes were 300–800 ml. Adsorbed volatiles were desorbed at 350°C directly in the injection port of the GC onto the gas-chromatographic column.

Desorption time was 10 min with 5 ml He min^{-1}. The GC-column was held at -80°C during desorption.

GC–MS procedure

GC–MS was carried out under the following conditions.

Quadrupole-EI-CI-Mass Spectrometer Finnigan 4500 with Incos-Data-System and General Nova 3; NBS spectra library with 33000 mass spectra; ion source temperature 250°C; ionization energy 70 eV; GC-column 25 m Carbowax 20 M fused silica; carrier gas helium with 2 ml min^{-1}; splitless injection; temperature program from -80 to 50°C with 30°C min^{-1} and then with 2°C min^{-1} to 220°C. CI–MS with ammonia as reactant gas, forepressure 1.3 mbar; ion source pressure 1.3×10^{-5} mbar; all other parameters unchanged.

RESULTS AND DISCUSSION

Thermal oxidative stability by PDSC

Figure 1 demonstrates the exothermic thermal-oxidative degradation of an oil at 250°C and the determination of the induction time, x, or onset (min). Kinetic treatment has shown that the oxidative breakdown is probably a first-order reaction. Therefore, plotting ln x vs. the reciprocal measuring temperature gives a straight line (correlation coefficients $\geqslant 0.99$). Those x values which cannot be determined experimentally because the induction times are too low or too high, can thus easily be calculated. Figure 2 gives some of these straight lines as a function of the ageing time t_A(h) of a used turbine oil, showing the expected displacement to lower x values and very similar slopes [12,13]. This is not always the case; often the slope of the straight lines increases with the advanced ageing of the oils. Only a small increase in temperature leads to a breakdown of the oil.

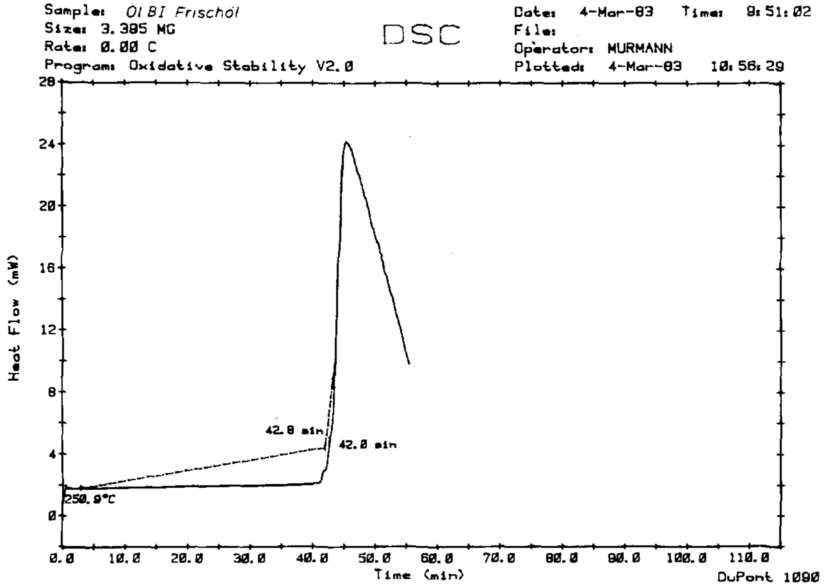

Fig. 1. Determination of the induction time x (extrapolated x') or onset (min) at 250°C.

An exceptional advantage of oil degradation in the DSC cell is the simulation of thin-film oxidation [15], which may be very important in working examples of oil degradation. Using the information given in Fig. 2,

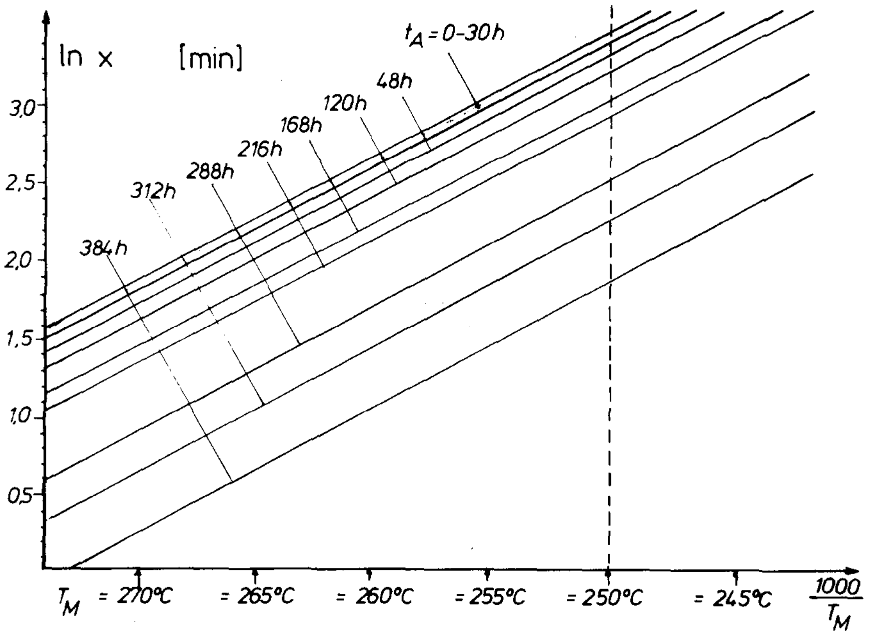

Fig. 2. Correlation between ln x and reciprocal measuring temperature, T_M (°C), as a function of the ageing time, t_A (h).

the effective ageing state of an oil can be demonstrated at any measuring temperature, T_M, as a function of the ageing time, t_A, and correlated with, e.g., analytically determined quantitative antioxidant concentrations [13,16]. These data may be used to identify engine malfunctions, in establishing optimal oil drain periods, or for assessing new oil formulations. In the latter case it would be of considerable interest to know the catalytic influence of metals present in turbine bearings on antioxidant depletion and oil degradation. This can also be investigated using PDSC and sample pans made from the metals in question [17].

Metal catalysis

Oil A

Figure 3 shows the catalytic influence of some relevant metals on the thermal-oxidative degradation as a function of the measuring temperature T_M (°C). The aluminium sample pan was used as a reference. Catalytic activity of the metal surface is somewhat dependant on the degradation temperature. At 260°C, e.g., the order of activity is

$$\mathrm{Fe} \gg \mathrm{Cr/Ni} \gg \mathrm{Zn} > \mathrm{Ta} > \mathrm{Ni} \gg \mathrm{Ti} > \mathrm{Al} > \mathrm{Mo}$$

Oil B

Oil B has the same ester base composition as oil A, but is inhibited with DODPA/OPAN instead of DODPA/Phtz.

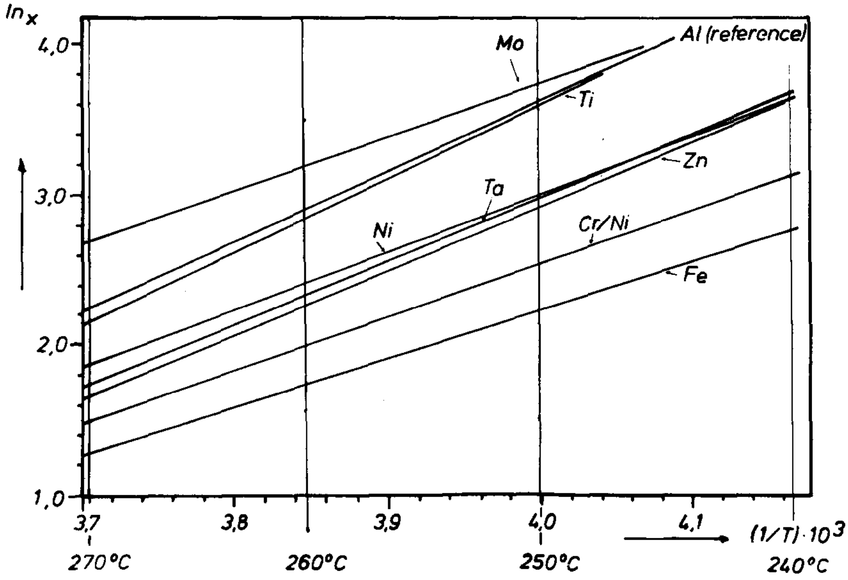

Fig. 3. Correlation between ln x and reciprocal measuring temperature, T_M (°C), catalytic influence of some metals on degradation of oil A.

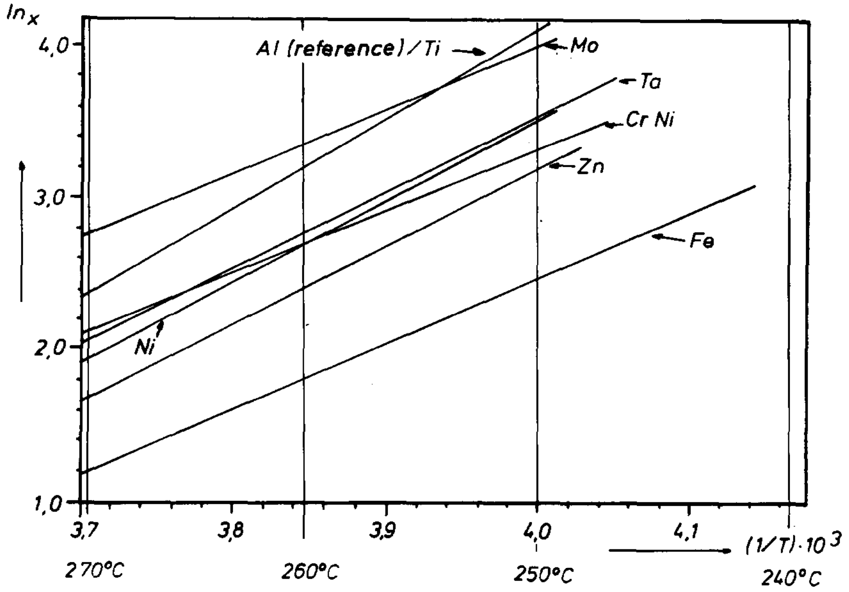

Fig. 4. Correlation between ln x and reciprocal measuring temperature, T_M (°C), catalytic influence of some metals on degradation of oil B.

Figure 4 shows that the catalytic influence of metal surfaces is not only affected by temperature, but also by antioxidants present. Again at 260°C, e.g., the order of activity is now

Fe $\gg$ Zn $>$ Cr/Ni, Ni $>$ Ta $\gg$ Al, Ti $>$ Mo

A preliminary investigation using electron spectroscopy for chemical analysis [18], has shown that the catalytically active material on the metal surface of our pans is in most cases the corresponding oxide (film thickness $\geqslant 5$–10 nm), e.g., Al_2O_3, MoO_3 and TiO_2. The nickel on the surface contains Ni_2O_3, but also some $Ni(OH)_3$ and Ni^0. The Cr/Ni steel surface is characterized by Fe^0, Fe_2O_3, Cr_2O_3 and traces of manganese.

GC–MS

The value of capillary GC–MS in organic trace analysis is well established. It is a very sensitive method capable of separating complex mixtures and identifying compounds in the picogram range. GC–MS in the EI or CI (NH_3) mode can be used very successfully to characterize degradation of lubricants and related materials in the DSC cell, thus correlating enthalpic changes with the chemical reactions occurring. This can be done using TENAX GC, an organic polymer based on poly-2,6-diphenylphenylenoxide and capable of adsorbing trace amounts of volatile organic compounds from gas streams [19]. Trapped volatiles can easily be desorbed at 300–350°C, in, e.g., the injection port of a GC–MS system, and subsequently analyzed.

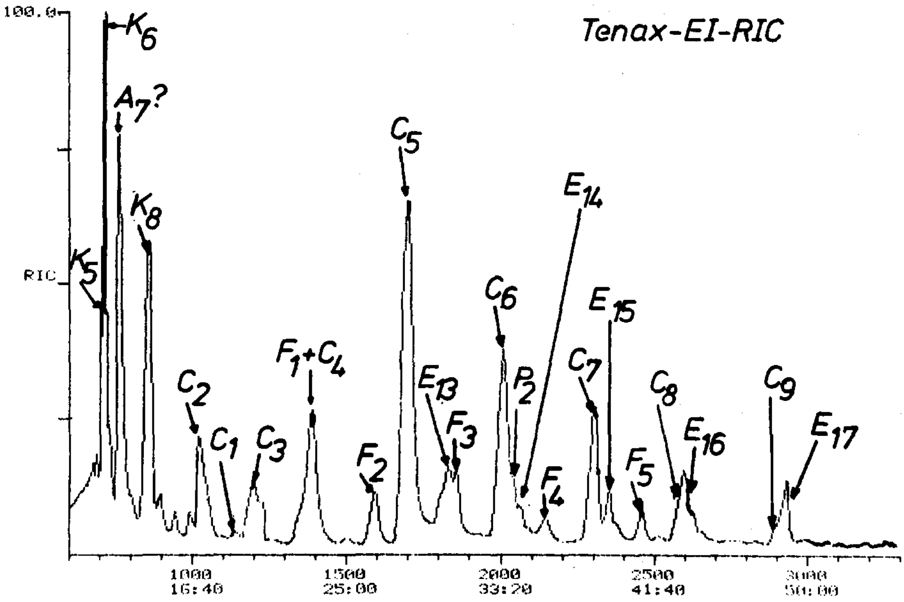

Fig. 5. Reconstructed ion chromatogram (EI-RIC) of the volatile degradation products adsorbed on TENAX GC for oil A.

Figure 5 shows as an example the reconstructed ion chromatogram (EI-RIC) of the volatiles produced from 3 mg aviation turbine oil at $T_M = 250°C$ (cf. Fig. 1). Detailed mass spectrometric analysis shows that the

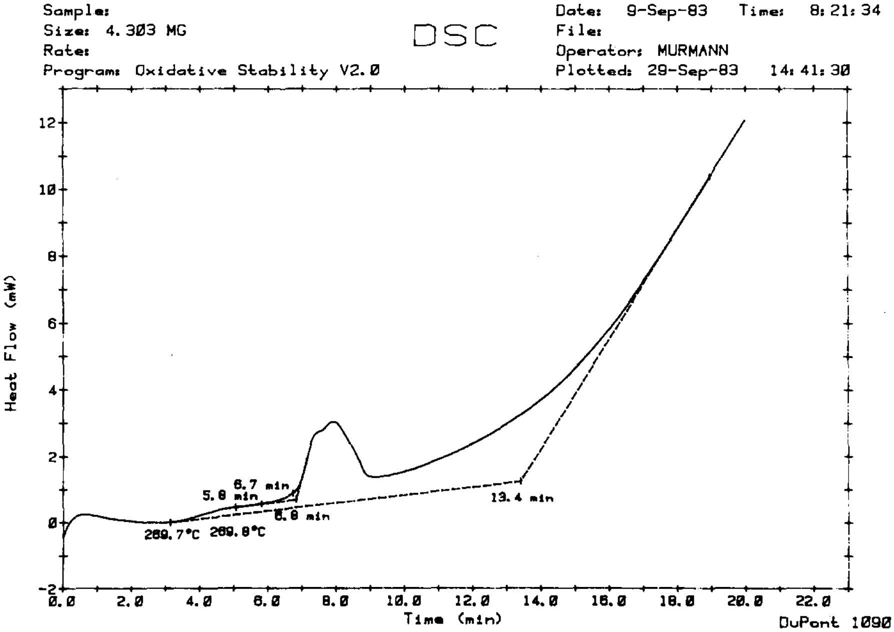

Fig. 6. PDSC diagram representing degradation of oil A on a Cd surface at 270°C.

ester base of the oil at this point already is degrading heavily. Characteristic degradation products are acids, esters, ketones, aldehydes and γ-, δ-lactones [20]. The main peaks in Fig. 5 are pentanone-2, hexanone-2 and octanone-2 (K5, K6, K8); peak A7 is probably heptaldehyde. Typical acids are C1–C9, and typical γ-lactones (furanones-2) are F1–F5. Only one δ-lactone, 6-ethyltetrahydropyranone-2 (P2) is seen. Characteristic thermal oxidative degradation products of these oils are also simple esters (designated E13–E17 in Fig. 5). One GC peak contains, as shown by MS, many isomeric species, e.g., E13 is a mixture of octyl pentanoate, heptyl hexanoate, hexyl heptanoate and pentyl octanoate. Esters are formed already in the early ageing state, probably via a Baeyer–Villiger oxidation of ketone precursors. The ability to do simultaneous investigations of the reactions taking place may be well recognized from Fig. 6, showing exothermic reactions of oil A on a Cd surface. No defined onset of degradation can be measured (see Fig. 1). Obviously, Fig. 6 reflects a change in degradation chemistry, which can be studied by a PDSC–GC–MS combination, as proposed.

CONCLUSION

The particular advantage we found in studying oil degradation and related problems with a DSC cell is that the cell can actually be used as a chemical reactor simulating thin film oxidation phenomena, investigating metal catalysis, behaviour of antioxidants on oil stability, etc. It is indeed a versatile tool in thermal and/or thermal-oxidative lubricant chemistry.

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