Thermo-Oxidative Behaviour of Perfluoropoly-alkylethers

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For high-temperature aircraft turbine engines in the next century, new, extremely stable lubricants will be required. The chemical class known as perfluoropolyalkylethers is well known for its good and wide range of temperature behaviour. This paper reports on investigations into the thermo-oxidative stability of these fluids at high temperatures. The work includes the influence of metals on the stability, and corrosion tests, of selected PFPAE oils. The results show the large influence of the chemical structure and of certain metals.

INTRODUCTION

To achieve greater efficiency in turbine engines, it will be necessary to increase the temperature in the combustion chamber of these engines. Consequently, engine oils that can withstand temperatures up to and beyond 300°C under oxidative conditions will be required. State-of-the-art turbine oils, based on alkyl esters, hydrocarbons, or polyphenyl ethers, cannot fulfil the demands for extreme thermo-oxidative stability and, simultaneously, good low temperature behaviour.[1]

Perfluoropolyalkylethers (PFPAE) have exceptional chemical and physical properties. They have good thermal stability.[2] Some compounds of this class also have excellent viscosity-temperature behaviour. PFPAE oils are considered, therefore, as possible base fluids for aircraft turbine engine applications.[3-13]

In this study, the authors have investigated the high temperature behaviour of PFPAEs with different chemical structures under oxidative conditions. Two main questions were studied:

- the influence of the chemical structure of PFPAE oils on their thermo-oxidative stability
- the interactions between metal, material, and PFPAE oils at high temperatures.

Figure 1 Schema of the micro-oxidation test
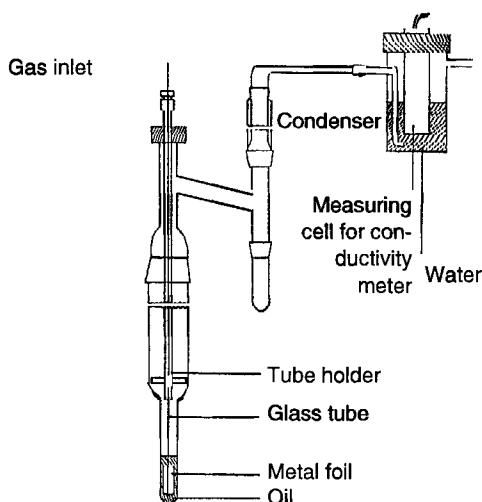
EXPERIMENTAL WORK

Apparatus

The price of PFPAE oils is high, and new synthetic products are currently only obtainable in small quantities. For these reasons, a new micro-oxidation test has been developed by the authors. A scheme of the glass apparatus is shown in **Figure 1**. The oil sample is placed in the lower and thinner part of the glass tube (inner diameter: 7 mm). The air is introduced through a glass capillary tube (outer diameter: 0.7 mm). The capillary tube is held in a glass tube. To investigate the interaction between metal and PFPAE oils, bent metal foils were placed in the oil sample. The oil samples were heated at the test temperature in a metal oven.

Gas inlet system

Combined mass-flow meters and regulators, based on heat conductivity, were used. This made it possible to adjust the air flow through the oil sample without regard to temperature or back pressure from the test apparatus. Accuracy

was better than 1% and reproducibility 0.2%. In addition, the air was dried in a gas-drying apparatus until the water content remaining was lower than 2 ppm. The air was blown through a standard glass capillary tube into the oil sample. This capillary tube provided a continuous flow of small gas bubbles of a reproducible size. A steady gas flow and good mixture with the oil sample were achieved thereby, and the oil sample was not ejected from the lower, thinner end of the glass tube.

Conductivity measurement

In extensive preliminary tests it was discovered that the oxidative decomposition of PFPAE oils permitted reproducible conductivity measurements. For this the outgoing airstream was taken into a conductivity measuring cell filled with distilled water. The decomposition products of the PFPAE oils clearly altered the conductivity of the water. Hence, the decomposition of PFPAE oils could be measured by means of the conductivity readings. The results were not affected by non-decomposed evaporated PFPAE oil.

Oils used

In this study, four commercial PFPAE oils were compared. These were technical mixtures of varying chain lengths. The structural and selected physical data are shown in **Table 1** and **Figure 2** (see overleaf). The criteria of selection for the oils were their varying chemical structures (**Figure 2**).

Table 1 Selected physical properties of the PFPAE oils tested

Oil	Viscosity at 40°C	Viscosity at 99°C	Mol. weight	Pourpoint	Spec. gravity (20°C)
Oil A	169 mm²/s	47 mm²/s	9500 g/mol	−66°C	1.85 g/cm³
Oil B	78 mm²/s	9.4 mm²/s	3000 g/mol	−35°C	1.90 g/cm³
Oil C	278 mm²/s	26 mm²/s	6250 g/mol	−36°C	1.9 g/cm³
Oil D	23 mm²/s	5.0 mm²/s	-	−70°C	1.86 g/cm³

Figure 2 Chemical structure of the PFPAE oils tested

Oil A $CF_3-O-(CF_2-O)_p-(CF_2-CF_2-O)_q-CF_3$ $p/q = 0.6 - 0.7$

Oil B $CF_3-O-(CF_2-O)_n-(CF-CF_2-O)_m-CF_3$ $m/n \sim 40$
$\qquad\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\qquad CF_3$

Oil C $R_{F_1}-O-(CF-CF_2-O)_n-CF_2-CF_3$ $R_{F_1} = CF_3-CF_2-CF_2-$
$\qquad\qquad\qquad |$
$\qquad\qquad\quad CF_3$

Oil D $R_F-O-(CF_2-CF_2-CF_2-O)_y-(CF_2-CF_2-O)_x-R_F$ $R_F = CF_3-CF_2-,$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = CF_3-CF_2-CF_2-$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad x < y$

Metals used

For the analysis of the interactions between the metal and the oil the following metals were employed: aluminium (Al), copper (Cu), nickel (Ni), iron (Fe), and silver (Ag). Metal purity was in each case above 99.95%. Metal foils were cut into 1.5×2.5 cm^2 strips and were folded around a triangular bar (each side, 5 mm) to form an equilateral triangular tube (length 2.5 cm). Subsequently, the bent foils were then cleaned several times with cyclohexane and acetone in an ultrasonic bath. Finally, they were dried and kept under vacuum before use.

Experimental procedure

The oil (3.6 g) was placed in the glass apparatus. The glass apparatus and the distillation flask were weighed to the nearest 1.0 mg, and the prepared metal foil to exactly 0.01 mg. The conductivity measuring cells were filled with 50 ml freshly distilled water before each experiment. The apparatus was heated to the test temperature in a preheated and thermostatically controlled oven. The air flow through the oil was maintained at 2 l air/h. The change in conductivity was recorded throughout the test. The test time was set at 24 h. After the test, the glass apparatus, the distillation flask, and the metal foil (after

Figure 3 Thermo-oxidative stability of PFPAE oils without metals. Weight loss of the oils after a test period of 24 h
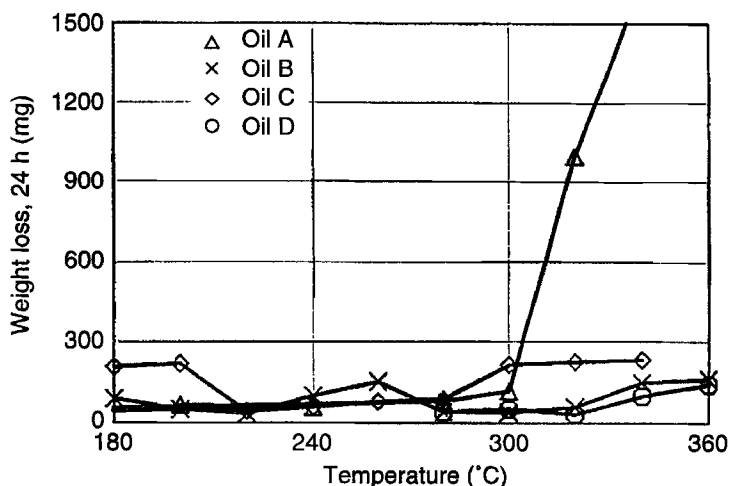
washing with trichlorotrifluoroethane) were reweighed, and the water from the conductivity cells was kept.

RESULTS

Thermo-oxidative stability of the PFPAE oils

The PFPAE oils were aged oxidatively in the temperature range from 180°C to 360°C. The weight loss in relation to test temperature after a 24 h test period is shown in **Figure 3**. It is composed of the sum of evaporation and splitting products of the PFPAE oils. Up to 360°C, the oils investigated showed only negligible loss, and, therefore, appear to be stable. One exception was oil A. Above 300°C, this oil showed a clear weight loss. In order to determine whether oxidative fission had taken place under these conditions, the conductivity measurements were examined.

The final conductivity readings, after the 24 h test, are given in **Figure 4** (see overleaf). Unlike the weight loss results, the oxidative degradation of oils A and B began above 260°C. However, the decomposition rate of oil B was clearly lower. Oil C was stable to a temperature of 280°C, and oil D up to

Figure 4 Thermo-stability of PFPAE oils without metals. Conductivity after 24 h test period in measuring cell water
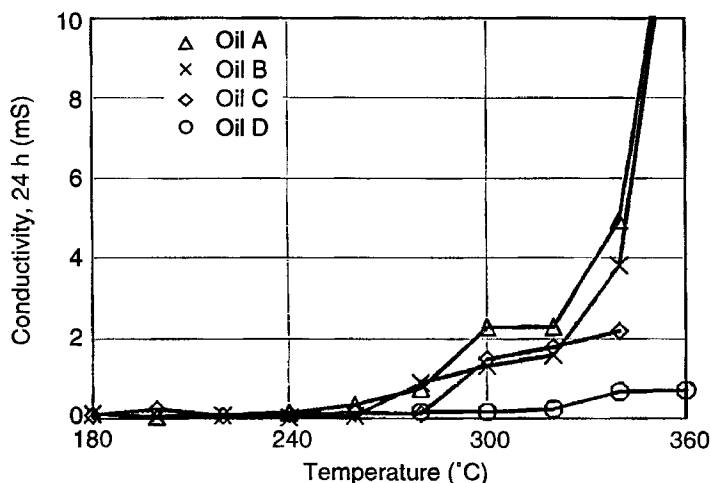
320°C. Unlike with hydrocarbon oils, in this study neither an autocatalytic acceleration nor an inhibition time could be found. Rather, the oils were stable, with respect to their chemical structures, up to a specific temperature (see above). Above these temperatures, the decomposition rates have been specified only by temperature and oil type. This decomposition rate, under the test conditions, is very low in all cases, particularly considering that many splitting products are highly aggressive.

Oils A and B have, in contrast to oils C and D, a CF_3-O- end group and an -O-CF_2-O- group in the molecule. In the literature,[3-13] these structural elements are agreed to be responsible for the inferior stability of such oils. The branching of the -O-CF_2-$CF(CF_3)$-O- group possibly offers a certain steric protection for the neighbouring -O-CF_2-O- group and may explain, therefore, the somewhat higher stability of oil B as opposed to oil A. Another structural reason may be the clearly lower number of -O-CF_2-O- groups in oil B as compared with oil A. In this case, the higher stability would be produced through the statistically lower number of 'points of fracture' in the molecule. Oils C and D do not contain -O-CF_2-O- groups.

Influence of metals on thermo-oxidative stability

The weight loss with respect to temperature is shown in **Figure 5** (see over-
leaf) for the metals analysed, Fe, Cu, Ni, Ag, and Al. It can be seen from the
graphs that Al and Fe clearly lower the oxidation stability of the PFPAE oils.
However, the chemical structure has a great influence as well. Again, oil A is
the least stable. Above 220°C, a decomposition in the presence of Al is ob-
servable. Fe and Cu are first effective above 260°C. Weight loss from oil B
can be seen with Fe above 280°C, from oil C only above 320°C, and, under
these conditions, oil D is almost stable. Ni and Ag have only a very slight ef-
fect on stability.

As in the series of tests without metals (see above), conductivity was also
recorded. The final conductivity after a 24 h test period with respect to tem-
perature and metal is shown in **Figure 6** (see p. 199) for oils A-D. According
to this, the metals decomposed the oils analysed in the sequence Al > Fe > Cu
> Ni = Ag. Oil A resisted catalysis by Al only up to a temperature of 220°C,
oil B up to 260°C, oil C up to 280°C, while oil D remained stable up to a tem-
perature of 320°C. A similar stability sequence results for the other metals.
Moreover, it was observed that oils B and C were similarly affected by Fe and
Al while oil D was more strongly decomposed by Fe than by Al. Nevertheless,
the temperature level of 320°C is already very high. Cu, Ni, and Ag had only
a slight effect on oils B-D.

It may be stated, in summary, that aluminium and iron reduce the thermo-
oxidative stability of PFPAE oils. The fluorides of Al and Fe are Lewis acids.
In the literature, Lewis acids are described as particularly active in the case of
PFPAE oils. The weakest positions in the molecules are the ether bonds.
Moreover, the -O-CF$_2$-O- group is especially susceptible. One reason may lie
in the steric vicinity of both ether bonds, which enables the metal catalyst to
act on both oxygen bonds simultaneously. In oil B the perfluoro-isopropyl
group can sterically protect one of the ether bonds. The better stability of oils
C and D can, therefore, be explained by the large distance between ether
bonds. In this case an individual catalyst molecule can no longer attack both
ether bonds simultaneously.

Analysis of the aged oils

The aged PFPAE oils and the water from the conductivity measuring cells
were analysed in order better to understand the chemical changes of the oils

Figure 5 Influence of metals on thermo-oxidative stability of PFPAE oils. Oil weight loss after a 24 h test period
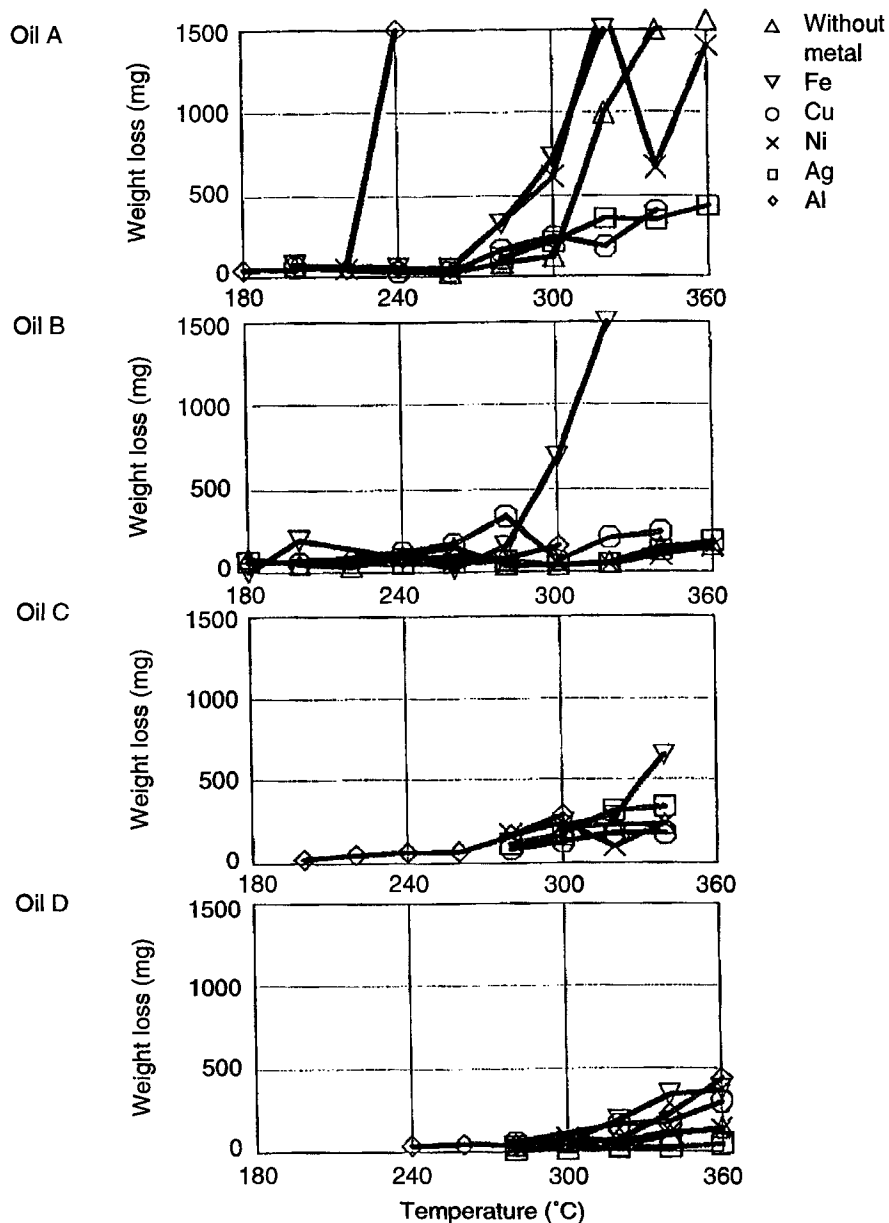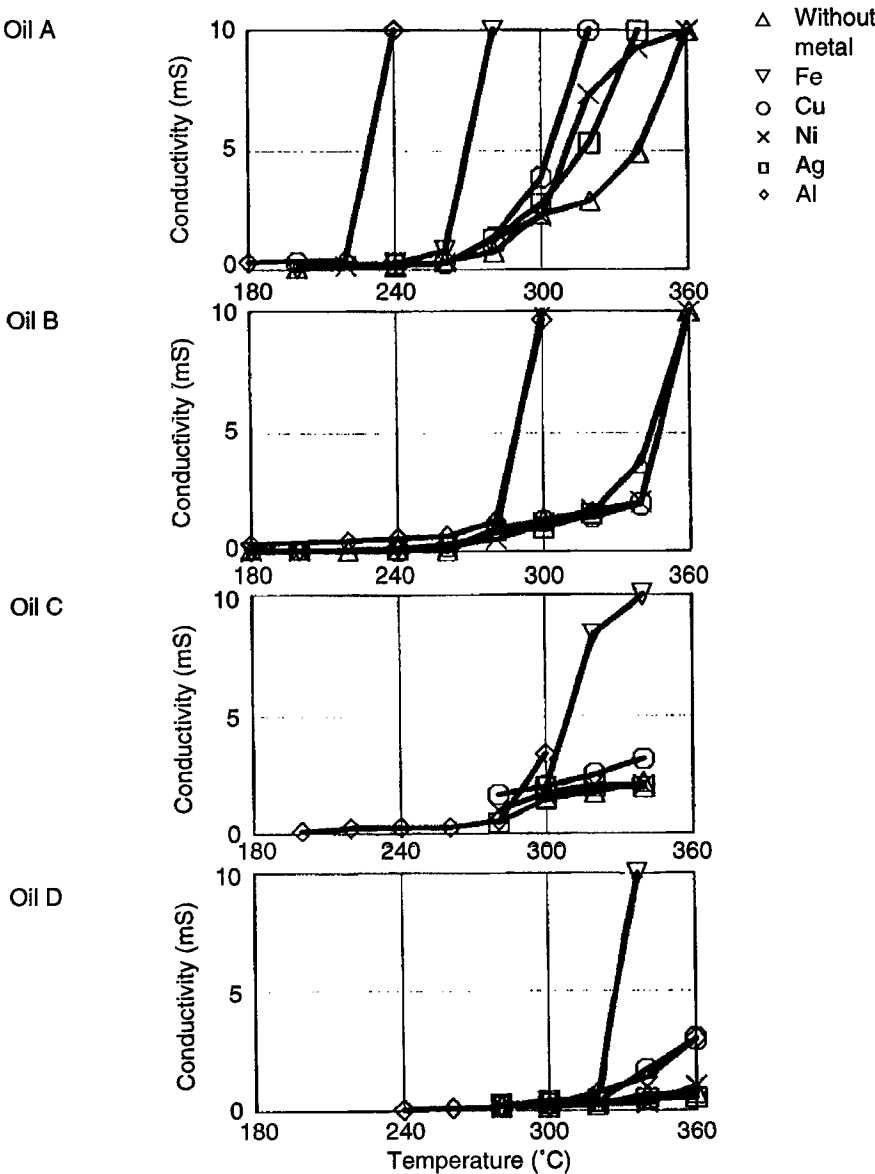
**Figure 6 Influence of metals on thermo-oxidative stability of PFPAE oils.
Conductivity after 24 h test period in measuring cell water**

under thermo-oxidative stress. The viscosity increase was in all cases insignificant (10%). Nevertheless, the oils aged with Al showed a viscosity decrease up to 5% above their respective decomposition temperatures.

In order to find the cause of the change in viscosity, selected aged oil samples were analysed for changes of molecular weight by means of gel permeation chromatography. No significant changes were found. Furthermore, the analysis using ^{19}F nuclear resonance spectroscopy showed no differences between processed and fresh PFPAE oils. Using infrared spectroscopy, new bands were found only in the region above 3200 cm^{-1}. These are characteristic of OH vibrations; however, the intensity was only low.

Additionally, selected samples of the water from the conductivity measuring cells were investigated with ion chromatography. Fluoride and trifluoroacetic ions were found. Hence, it can be deduced that the oxidised PFPAE oils were split into small molecules. These were distilled away, and show, in contrast to hydrocarbons, no tendency toward polymerisation. Further, viscosity increase took place through a slight distillation-caused contraction in molecular weight distribution in the lower molecular range and not through polymerisation of the oils, as is common with conventional hydrocarbon oils.

Influence of the PFPAE oils on metals

The weight change of the metal foils with respect to PFPAE oils and temperature is shown in **Figure 7**. No weight decrease was found for the metals studied in any of the tests. This reflects the poor solubility of PFPAE oils for polar compounds. Therefore, once formed, the oxidation or corrosion products could not be dissolved from the metal surface. Nevertheless, the structure of the PFPAE oils had a clear influence on the oxidative and corrosive protection of the metals. This runs essentially parallel to the thermo-oxidative stability of the oils.

With scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), further investigations were carried out on selected metal foils. An iron foil after exposure to thermo-oxidative stress in oil B at 320°C is shown in **Figure 8** (see p. 202). The growth of a porous layer on the metal surface can be seen, but the characteristic corrosion holes are absent. The EDX analyses (**Figure 9**, p. 202) show a mixed oxide-fluoride layer, the oxide part being the greater. Therefore, it must be considered that a major part of the layer results from direct oxidation of the metal surface. Among the metals investigated, Al, Cu, and Fe were hardly attacked, whereas Ni and Ag were almost inert.
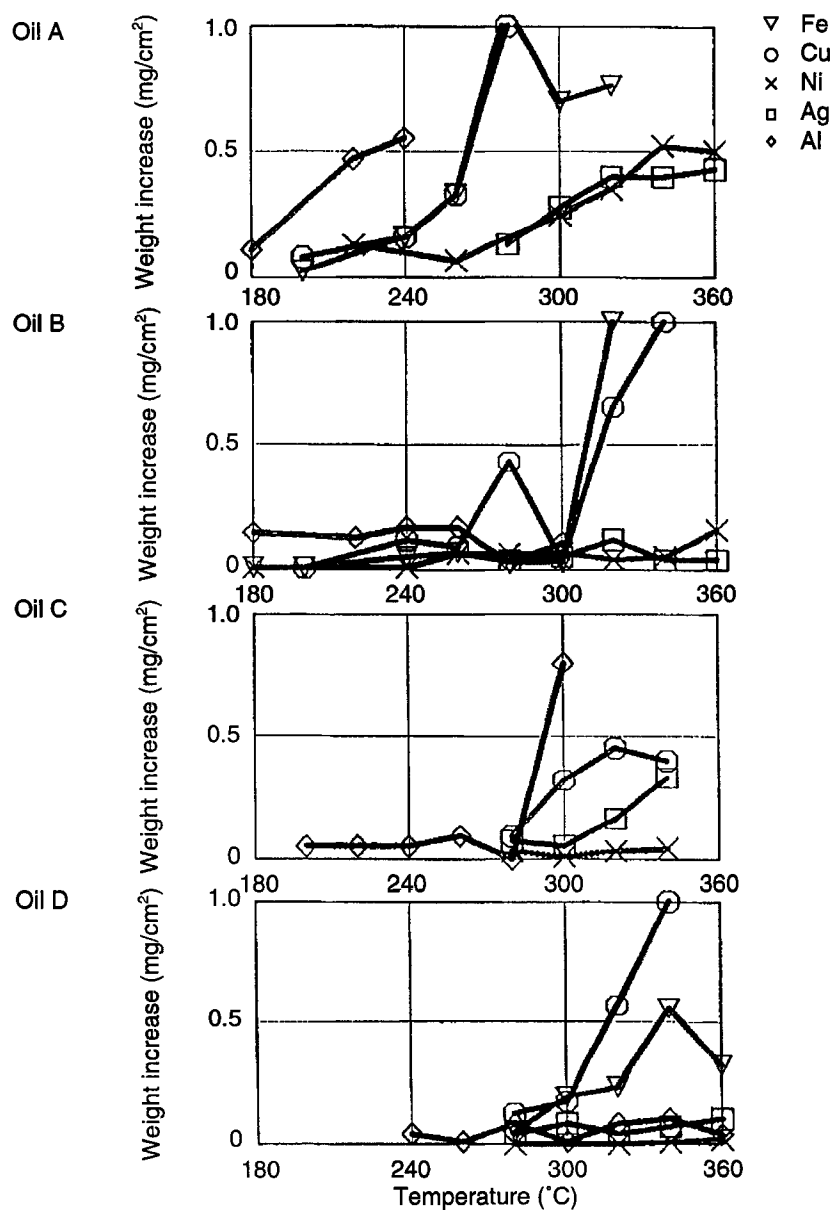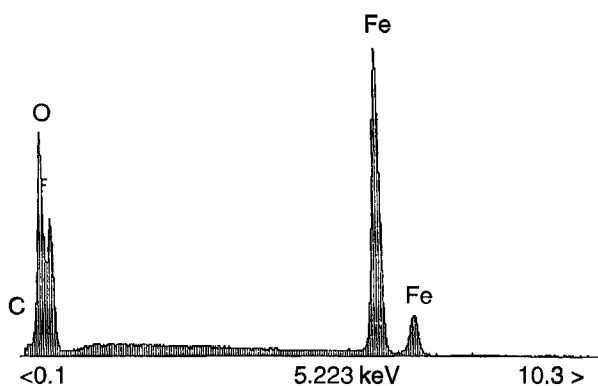
Figure 7 Influence of PFPAE oils on metals at high temperatures and in oxidative conditions

**Figure 8 Reaction layer on iron, formed under oil B.
Test time: 24 h, temp. 320°C**

**Figure 9 EDX analysis of a reaction layer on iron formed under oil B.
Test time: 24 h, temp. 320°C**

SUMMARY AND CONCLUSIONS

PFPAE oils have notable chemical behaviour. Even under oxidative conditions, and in the presence of metals, their operational thermo-oxidative limits are considerably higher than conventional oils. However, the chemical structure of the PFPAE oils is of importance. Structures without -O-CF_2-O- groups offer improved stability. Moreover, a strict linear structure of the perfluoro chains seems to be better than branched perfluoro-isopropyl groups.

In contrast to present oils based on hydrocarbons or esters, with PFPAE oils polymerisation products are not formed even beyond the thermo-oxidative stability limit. But, in that case, products evolve which form hydrofluoric acid in the presence of water. Therefore, if such oils are used, care must be taken not to exceed these temperatures. It should be noted that, as the PFPAE oils reacted with the glass wall of the apparatus at high temperatures, it might be possible to increase the upper operational temperature limit by careful selection of proper materials.

Under test conditions, a mixed oxide-fluoride layer is found on the metal surfaces. Its thickness is related to the catalytic activity of the metals on the PFPAE oils. Here the Lewis acid formers Al and Fe are especially harmful. For this reason an intensive investigation of the interaction between oil and metal is required. Other questions opened up are whether further extension of perfluorinated alkyl chains leads to increased thermo-oxidative stability, and whether it is possible to find high pressure (EP) and antiwear (AW) additives for these liquids, and their extreme temperature applications. PFPAE oils can be enhanced in stability by additives.[14]

References

1. Koch, B., 'Thermal stability of synthetic oils in aviation applications', *J. Synth. Lubr.*, 6, 4, 275-84 (1990).
2. Koch, B., Jantzen, E., 'Thermo-Oxidationsstabilität von Oelen in der Luftfahrt', *Tribologie und Schmierungstechnik*, 36, 6, 293-6 (1989).
3. Snyder, C.E., Gschwender, L.J., and Tamborsky, C., 'Linear polyperfluoroalkylether-based wide-liquid-range high-temperature fluids and lubricants', *Lubrication Engineering*, 37, 6, 344-9 (1981).
4. Sianesi, D., and Fontanelly, R., 'Perfluoro polyethers. Their structure and reaction with aluminium chloride', *Die Makromolekulare Chemie*, 102, 115-24 (1967).
5. Chandler, W.L., Lloyd, L.B., Farrow, M.M., Burnham, R.K., and Eyring, E.M., 'Titanium corrosion by hot perfluoropolyether', *Corrosion*, 36, 3, 152-5 (1980).
6. Carré, D.J., 'Perfluoropolyalkylether lubricants under boundary conditions: iron catalysis of lubricant degradation', *J. Synth. Lubr.*, 6, 1, 3-15 (1989).

7. Snyder, C.E., and Dolle, R.E., 'Development of polyperfluoroalkylethers as high-tempera-ture lubricants and hydraulic fluids', *ASLE Trans.*, **19**, 3, 171-80 (1976).
8. Carré, D.J., 'Perfluoropolyalkylether oil degradation: inference of FeF_3 formation on steel surfaces under boundary conditions', *ASLE Trans.*, **29**, 2, 121-5 (1986).
9. Carré, D.J., and Markowitz, J.A., 'The reaction of perfluoropolyalkylether oil with FeF_3, AlF_3 at elevated temperatures', *ASLE Trans.*, **28**, 1, 40-6 (1985).
10. Paciorek, K.J.L., Kratzer, R.H., Kaufman, J., and Nakahara, J.H., 'Thermal oxidative stud-ies of poly(hexafluoropropene oxide) fluids', *Journal of Applied Polymer Science*, **24**, 1397-411 (1978).
11. Paciorek, K.L., Kratzer, R.H., Kaufman, J., and Nakahara, J.H., 'Determination of fluoro-carbon ether autoxidative degradation mechanisms', AFML-TR-77-150.
12. Jones, W.R., Paciorek, K.J.L., Harris, D.H., Smythe, M.E., Nakahara, J.H., and Kratzer, R.H., 'The effects of metals and inhibitors on thermal oxidative degradation reactions of un-branched perfluoroalkyl ethers', *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 417-20 (1985).
13. Zehe, M.J., and Faut, O.D., 'Acidic attack of perfluorinated alkyl ether lubricant molecules by metal oxide surfaces', *Tribology Trans.*, **33**, 4, 634-40 (1990).
14. Srinivasan, P., Corti, C., Montagna, L., and Sarelli, P., 'Soluble additives for perfluorinated lubricants', *J. Synth. Lubr.*, **10**, 2, 143 (1993).