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Biodegradable lubricants—studies on thermo-oxidation of metal-working and hydraulic fluids by differential scanning calorimetry (DSC)

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Abstract

In continuation of our study of the thermal-oxidative degradation of lubricants using PDSC, we investigated the biodegradable metal-working and hydraulic fluids that are available on the European market. Isothermal onset times of oxidation were measured at different sample temperatures and plotted against the reciprocal temperatures, giving straight ageing lines which were used to differentiate between the thermal-oxidative stabilities of the oils.

The stabilities of metal-working oils and hydraulic fluids vary over a wide range. Synthetic ester oils are more stable than vegetable-based fluids; however, our work demonstrates that the latter can be improved by selected antioxidants to yield equal or even better thermal-oxidative stabilities.

Measurements conducted on steel surfaces show a strong catalytic influence compared to an inert aluminium (Al_2O_3) surface for both fluids.

We also investigated the stabilities of laboratory-aged hydraulic fluids (ASTM-D-2893). The results, by PDSC alone or in combination with conventional oxidation tests, show that the ageing behaviour of biodegradable lubricants can be assessed effectively.

Commercial products are by no means of equal quality in this respect. In our opinion, single PDSC measurement could offer many advantages over the conventional oxidation tests used, such as the Baader test (DIN 51554) or the Rancimat test.

Typical results for commercial products based on rapeseed oil and synthetic esters are presented.

Keywords: Biodegradable lubricants; DSC; Thermal-oxidative stability

1. Introduction

During recent years, interest in Europe in environmentally friendly or readily biodegradable lubricants based on vegetable oils and synthetic esters has increased

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considerably [1–3]. The properties of vegetable oils are determined by their fatty acid composition. A high content of linolic/linolenic acid decreases thermal-oxidative stability, whereas a higher proportion of long-chain saturated fatty acids leads to inferior cold flow behaviour.

Synthetic esters are also very satisfactory from an environmental point of view because of their biodegradabilities and ecotoxicological properties. Products from oleo chemicals are of particular interest in the production of esters at acceptable costs. Trimethylolpropane esters, neopentylpolyol esters and also complex esters are possible base oil candidates.

Thermal-oxidative stability is still the most difficult property to determine in vegetable oils and synthetic esters made from oleo chemicals containing unsaturation. Not all vegetable oils have the same properties; moreover, for economic reasons a certain oil type, e.g. rapeseed oil, can be obtained in different grades by modern refining techniques. Also, using advanced plant-breeding techniques, vegetable oils which exhibit excellent thermal-oxidative stability, e.g. high oleic acid sunflower oil, are becoming available. Antioxidants must still be used with both base fluids and they must also be environmentally friendly.

In continuation of our study of the thermal-oxidative degradation of lubricants using pressure differential scanning calorimetry (PDSC), we investigated the biodegradable metal-working oils and hydraulic fluids on the European market. The applicability of PDSC for this work has been shown in a number of papers [4,5]. In addition to the thermal-oxidative stabilities of fresh oils on aluminium and steel surfaces, we also measured hydraulic oils laboratory-aged at 100°C (ASTM-D-2893). The results are reported in this paper.

2. Experimental

2.1. Oils

Commercial metal-working and hydraulic fluids from different suppliers were screened for their base fluid composition using a mass spectrometric technique, namely direct exposure probe chemical ionization mass spectrometry (CI(NH_3)-MS) [6,7].

The metal-working oils were based on rapeseed oil and modified rapeseed oil (samples A–E). The hydraulic fluids were based on rapeseed oil (samples A–F) and trimethylolpropane trioleate (samples B^I–D^I and G^I–I^I), but one neopentylglycol ester (sample E^I) and one ester mixture (sample F^I) were found. Unsaturation was always present to a variable degree.

Metal-working oils:	samples A–E	
Hydraulic fluids:	rapeseed oil based:	samples A–F
	trimethylolpropane trioleate	samples B^I–D^I and G^I–I^I
	based and other composition:	E^I–F^I

2.2. PDSC standard procedure

PDSC was carried out using a DuPont 1090/2000 Thermal Analyzer with a DuPont pressure differential scanning calorimeter cell under the following conditions: isothermal mode; sample temperatures from 130 to 190°C; sample mass, 3 mg; standard sample pan, aluminium and home-made steel pans; synthetic air with 7 bar pressure; correlation of ln t_x (induction time/onset time of oxidation) with t^{-1} (in $°C^{-1}$) by linear regression.

3. Results and discussion

3.1. Thermal-oxidative stability of virgin commercial metal-working oils

Fig. 1 illustrates the exothermic thermal-oxidative degradation of a biodegradable oil at 185°C and the determination of the induction time t_x (extrapolated) or onset time of oxidation in minutes. In most cases the onset of oxidation is sharp and well-defined, except with uninhibited or very slightly inhibited products. The isothermal onset time t_x was measured for the different types of oil at four or five different temperatures in the range 130 to 190°C. Plotting ln t_x against the reciprocal sample (ageing) temperature gives a straight line. The t_x values that cannot be determined experimentally because the induction times are too low or too high can thus be easily calculated. Fig. 2 shows some of these straight lines for selected commercial oils A–E on an aluminium surface

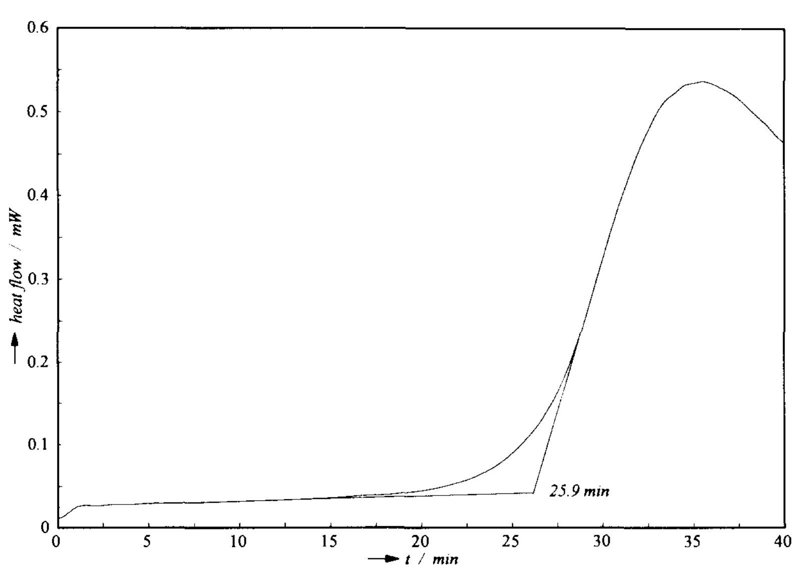

Fig. 1. Determination of the induction time t_x (extrapolated) or extrapolated onset time of oxidation t_x (in min) at 185°C of a biodegradable oil (aluminium surface).

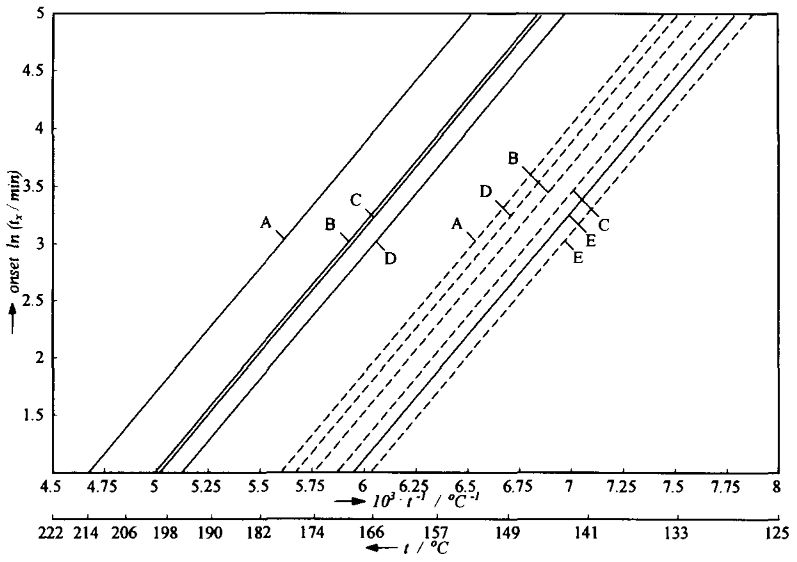

Fig. 2. Correlation between $\ln(t_x/\text{min})$ and reciprocal measuring temperature t^{-1} (in °C^{-1}) for rapeseed-oil-based and modified commercial metal-working oils (A–E) on aluminium (———) and steel (-------) surfaces, demonstrating the catalytic influence on oil oxidation.

(———). Oils D and E are rapeseed-oil-based; oils A–C are modified rapeseed oil products containing 2-ethylhexylester. The thermo-oxidative stabilities vary over a wide range as demonstrated in Fig. 2. However, lower stabilities are also acceptable because this property is of minor importance in the case of cutting oils in contrast to that of hydraulic fluids.

In assessing new oil formulations, especially hydraulic fluids, it is of considerable interest to know the catalytic influence of different metal surfaces on antioxidant depletion and oil oxidation. This can also be investigated using PDSC and sample pans made from the metals in question. Fig. 2 also demonstrates the strong influence of a steel surface (-----) compared to an inert aluminium surface (active material is Al_2O_3) for metal-working oils A–E. The onset of oxidation is considerably reduced.

3.2. *Thermal-oxidative stability of virgin commercial hydraulic fluids*

Figs. 3 and 4 show our results for commercial hydraulic fluids. Some oils are rapeseed-oil-based (Fig. 3, A–F) and some are synthetic esters (Fig. 4, B^I–I^I). In this case as well, the thermal-oxidative stabilities vary over a wide range. As expected, synthetic ester oils are more stable than vegetable-based fluids, but the latter can be improved effectively by selected antioxidants to have equal or even better thermo-oxidative stabilities. In the case of hydraulic fluids, we have studied the influence of a steel surface in detail [8, 9]. The results show that the catalytic influence on oxidation is determined by base fluid and antioxidant/metal passivator selection. The refining grade of rapeseed oil is very important and affects additive action.

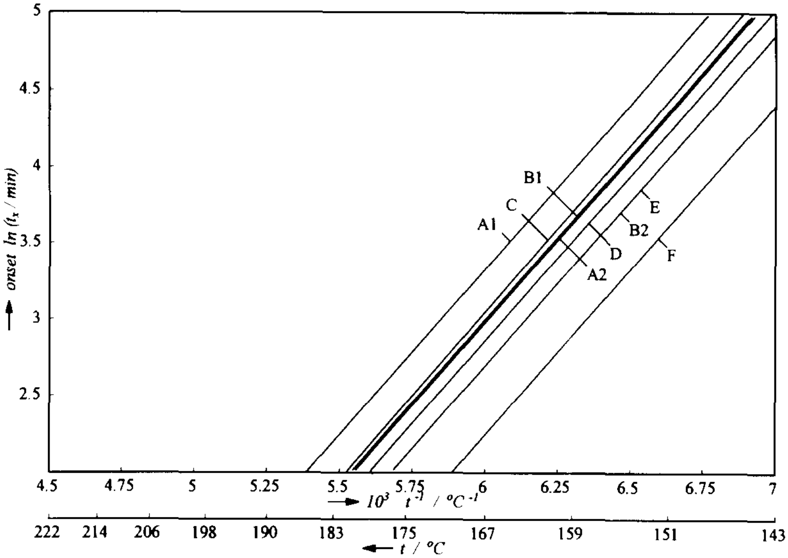

Fig. 3. Correlation between ln(t_x/min) and reciprocal measuring temperature t^{-1} (in °C^{-1}) for selected commercial rapeseed-oil-based hydraulic fluids (A–F) on an aluminium surface; A1 and A2, B1 and B2 are different formulations from the same supplier.

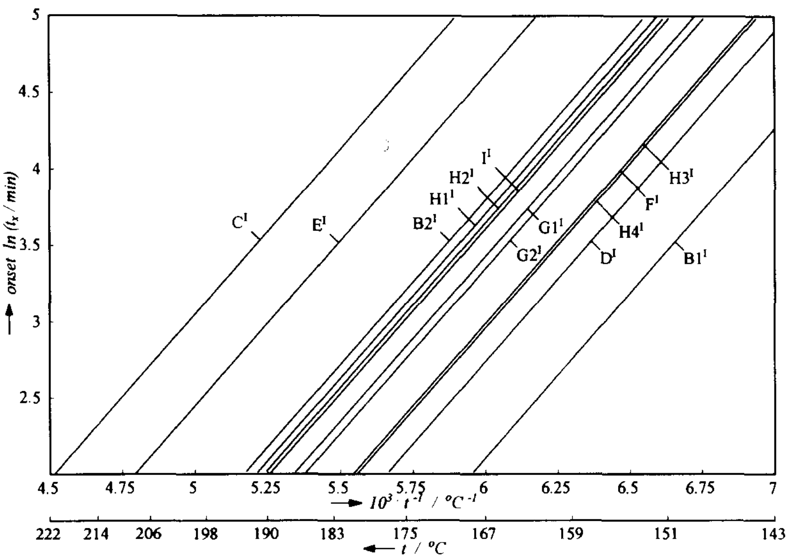

Fig. 4. Correlation between ln(t_x/min) and reciprocal measuring temperature t^{-1} (in °C^{-1}) for synthetic-ester-based hydraulic fluids (B^I–I^I) on an aluminium surface: A, vegetable; A^I, synthetic brand from the same supplier.

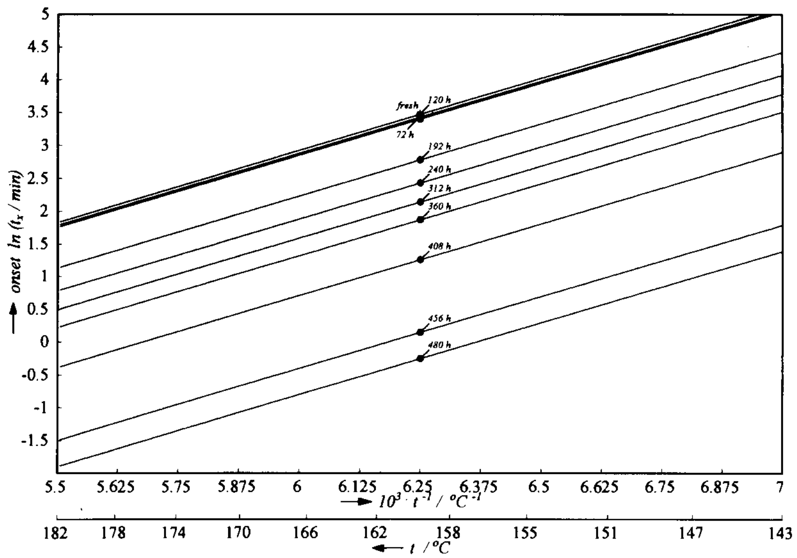

Fig. 5. Correlation between $\ln(t_x/\text{min})$ and reciprocal sample temperature t^{-1} (in °C^{-1}) as a function of the ageing time t_A (in h) (for details see text) for rapeseed-oil-based hydraulic fluid on an aluminium surface.

3.3. Thermal-oxidative stability of laboratory-aged commercial hydraulic fluids

Selected hydraulic fluids of different composition were aged according to ASTM-D-2893 at 100°C for up to 1700 h in the absence of metals. PDSC onset determinations on an aluminium surface were made as a function of the ageing time t_A (in h). Fig. 5 shows a typical PDSC result for a rapeseed-oil-based hydraulic fluid. Up to $t_A = 120$ h, there is no distinct decrease in thermo-oxidative stability, followed by a gradual breakdown. At a sample temperature of 160°C, the onset of the virgin oil of about 33 min is reduced to only 1 min after 456 h of ageing. Even at the very low temperature of 120°C, no reproducible onset determination is possible: in this state, the antioxidants are depleted and there is a viscosity increase of about 100%. In addition to measuring the viscosity and acid number increase during the ASTM-D-2893 oxidation test, it is advantageous to determine PDSC onsets because they correlate with the effective antioxidant concentrations in the aged oil.

4. Conclusion

More detailed work [10] shows that the ageing behaviour of biodegradable lubricants, especially hydraulic fluids, can be assessed effectively by PDSC alone or in combination with conventional oxidation tests (requested by a specification). Commercial products are by no means of equal quality in this respect. In our opinion, single PDSC measurement could offer many advantages over the conventional oxidation tests used, such as the Baader test (DIN 51554) or the Rancimat test, provided a correlation of the results exists, which still has to be investigated. The most important advantages are a short analysis time, good reproducibility and the possibility to assess rapidly the catalytic influences of different contact surfaces.

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