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Evaluation of sodium stearate as a synergist for arylamine antioxidants in synthetic lubricants

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Abstract

Differential scanning calorimetry (DSC) was employed to evaluate the performance of an ester lubricant containing sodium stearate. In the isothermal DSC oxidation test, sodium stearate is an effective synergist for arylamine antioxidants such as *p,p'*-dioctyldiphenylamine (DODPA). When combined with arylamine antioxidants, sodium stearate can also effectively reduce the increases in viscosity and acid number of the ester oil in oxidation–corrosion tests. The electron paramagnetic resonance (EPR) results indicated that sodium stearate can reduce the free radical contents in the oxidized oil in the presence of arylamine antioxidants.

Keywords: Antioxidant; DSC; Sodium stearate; Synthetic lubricant

1. Introduction

Oxidation stability is a major requirement for synthetic lubricants, especially for those used in aircraft gas turbine engines, owing to the high-temperature oxidative environment. Organic esters represent one of the largest groups of synthetic lubricants in use today. The principal use of these fluids is still in the lubrication of jet engines for military and commercial aricraft. Two classes of esters are defined by Military Specifications MIL-L-7808 and MIL-L-23699. Thermal-oxidative stability is one of the most important parameters responsible for the maximum service life of aviation turbine oils.

Davis and Thompson reported the synergistic effect of alkali metal salts of carboxylic acids with arylamine antioxidants in improving the oxidation stability of synthetic

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lubricants [1]. By using the 218°C oxidation–corrosion test, they showed that alkali metal salts of carboxylic acids, substituted phenols and the partial amide of ethylenediaminetetracetic acid (EDTA) possessed high activity as synergists for arylamine antioxidants in ester-type synthetic lubricating oils. Chao et al. reported that alkali metal salts of perfluorobutyric acid and other acidic compounds, when used with *N*-phenyl-α-naphthylamine (PANA) and/or *p,p*′-dioctyldiphenylamine (DODPA), were outstanding in reducing the oxygen absorption of ester oils [2].

A large number of laboratory tests have been developed for the investigation of oil oxidation stability and these have been reviewed by Hsu [3]. The differential scanning calorimetry (DSC) technique is now widely used to screen lubricant and a number of examples of this application have been reported [4–7]. It is probably the most suitable test for screening high-temperature lubricants, being fast, repeatable and capable of application at higher temperatures than is practicable for blown oxidation tests. In addition, as DSC is a thin film test, it alleviates the problem of oxygen diffusion and in some respects may more closely simulate the oxidation of a lubricant under boundary lubrication conditions. However, the DSC estimation of the effectiveness of alkali metal compounds as synergistic antioxidants with arylamine antioxidants has not been reported.

In this paper, isothermal DSC and an oxidation–corrosion test were employed to evaluate the performance of synergistic sodium stearate–arylamine antioxidant systems in a pentaerythritol ester. Free radical contents of the oxidized oils were determined to explain the antioxidation synergistic effect of alkali metal compounds.

2. Experimental

2.1. Test basestock and additives

The base fluid used in testing the antioxidants was a pentaerythritol ester of a mixture of C_5–C_{10} fatty acids, which was commercially available. Antioxidants such as PANA, DODPA, metal deactivator benzotriazole (BTA) and sodium stearate were purchased from commercial sources. All the additives were of more than 98% purity.

2.2. DSC standard procedure

All DSC experiments were made on a Perkin-Elmer 7-series thermal analysis system. The DSC experiment involves heating a thin film of oil sample on an aluminum pan in an oxygen atmosphere and detecting the exotherm corresponding to the onset of rapid and accelerating oxidation. This was carried out in the isothermal mode where the temperature is held constant and the elapsed time to the onset of oxidation (oxidative induction time) is measured. A longer oxidative induction time (OIT) is indicative of an improved oxidation stability.

Samples weighed 2.00 mg (± 0.05 mg) and the temperature was 240°C. Ultra-pure oxygen was used. The oxygen flow rate was 80 mol min^{-1}. The induction period from the isothermal experiments was obtained by extrapolation of the front edge of the exothermic peak to the baseline.

2.3. *Oxidation–corrosion tests*

The oxidation and corrosion tests were conducted at 240°C according to Federal Test Method Standard 791b Method 5307 with minor modifications. They generally involved the bubbling of dry air at 167 ml min^{-1} through 250 ml of test oil in the presence of six metals (Fe, Ag, Al, Mg, Cu, Ti) and determining the changes in metal weight and the viscosity and acid number of the oil.

2.4. *Free radical determination*

Free radical contents of the oxidized esters were directly determined using electron paramagnetic resonance (EPR) spectrometer.

3. Results

Sodium stearate was added separately at 0.1% concentration to the ester basestock containing 1% DODPA, and the inhibited fluids were evaluated by isothermal DSC at 240°C. The results are shown in Figs. 1 and 2 which demonstrate the exothermic

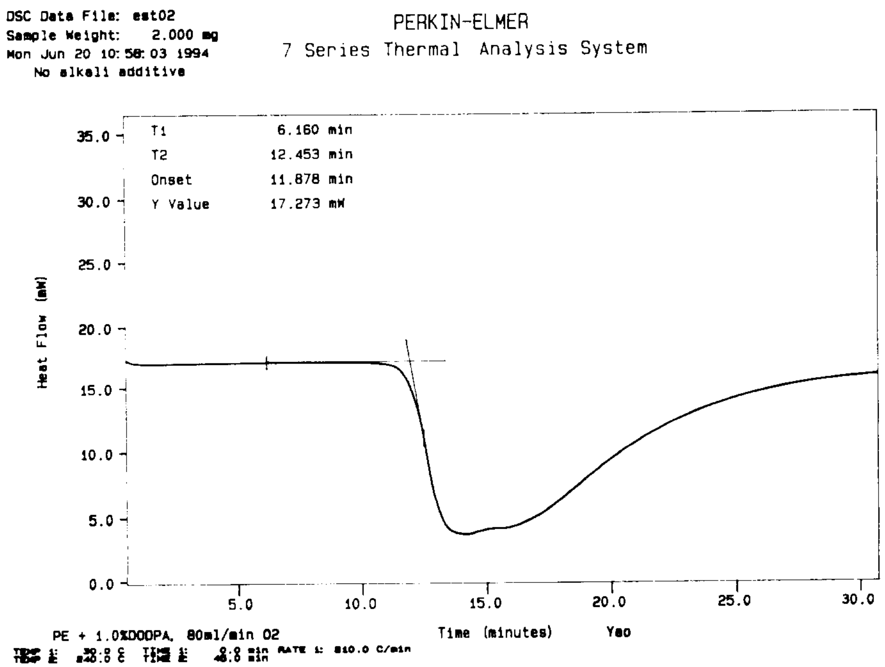


Fig. 1. DSC signal of the oxidation of the ester in the presence of DODPA.

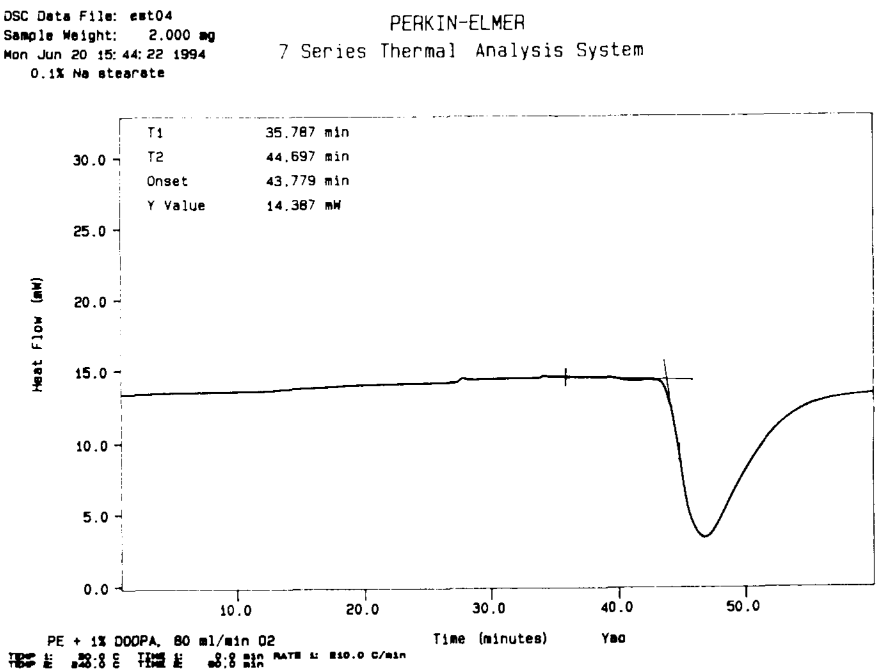


Fig. 2. DSC signal of the oxidation of the ester in the presence of DODPA and sodium stearate.

thermal–oxidative degradation of the ester without sodium stearate and the determination of OITs. Thus, 1% DODPA provided an OIT of 11.88 min, but the combination of 1% DODPA with 0.1% sodium stearate gave an OIT of 43.78 min. Although sodium stearate alone possesses no antioxidation activity in ester lubricants [1, 2], it can enhance the effectiveness of arylamine antioxidants.

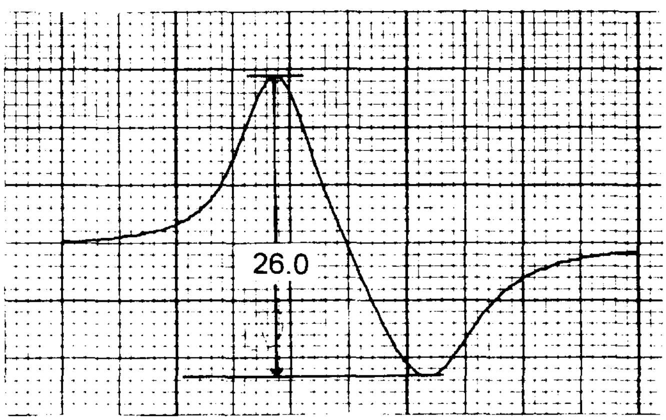
The effectiveness of sodium stearate as a synergistic antioxidant to PANA and DODPA was also demonstrated in the oxidation–corrosion test. Data are shown in Table 1 which show that 0.06% sodium stearate substantially reduced the increases in viscosity and acid number. The changes in metal weight are not reported in Table 1 due to no obvious metal corrosion both with and without sodium stearate in the oils.

The long-lived free radicals generated in the oxidized oils above were measured by an EPR spectrometer. The results are shown in Figs. 3 and 4. From these figures one can see that sodium stearate kept the free radical concentrations at low levels in the oxidized ester. In the presence of sodium stearate, the EPR signal strength was 3.15×10^{-5} (relative units) after 48 h of oxidation at 240°C, compared with 3.25×10^{-4} in the ester containing no sodium stearate in the same period. So sodium stearate can reduce the free radical content in the oxidized oil with arylamine antioxidants present.

Table 1
240°C Oxidation–corrosion test results.[a] Effect of sodium stearate

Base formulation		
Ester		97.90
PANA		1.00
DODPA		1.00
BTA		0.10
Oxidation inhibitor, mass%	**Viscosity increase, 40°C, %**	**Acid no. increase**
None	34.0	4.11
Sodium stearate, 0.06	23.7	1.57

[a] Test conditions: 48 h, 167 (ml air) min^{-1}.



8.0 X 10^4 times magnified

Fig. 3. EPR signal of the oxidized ester in the presence of PAN and DODPA.

4. Discussion

Scant literature information is available to explain the synergistic effect of alkali metal compounds. Davis and Thompson suggested three possible mechanisms [1]. Firstly, they propose that alkali metal salts direct the base oil to form oxidation products other than acid or sludge. But this means that they do not change the rate of oxidation. Our data on the isothermal DSC test clearly indicate that the rate of oxidation was greatly reduced. Secondly, they suggest the formation of complexes which are more potent antioxidants than the original material. We believe this is a definite possibility. Thirdly, they believe that the salts may form free radicals or

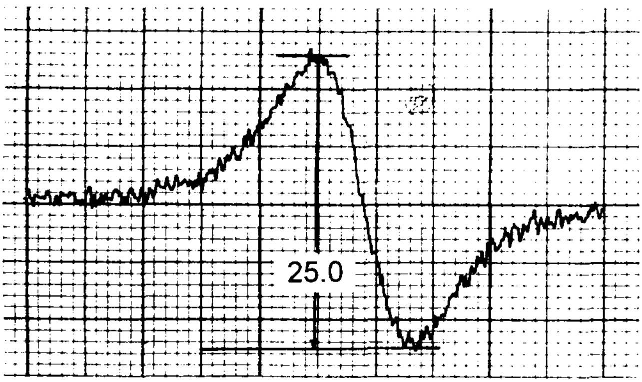


Fig. 4. EPR signal of the oxidized ester in the presence of PAN, DODPA and sodium stearate.

catalyze the antioxidants to form free radicals and interfere with autoxidation, with which the EPR data did not agree. In our EPR observation, the free radical contents in the oxidized oils were obviously reduced by the introduction of sodium stearate. Moreover, Chao et al. [2] suggested that the alkali metal ions can coordinate with the N atoms of the arylamine antioxidants and exert a shielding effect so that effectiveness of the arylamine antioxidants is improved. We tend to agree with this opinion (the coordination effect).

The pattern and structure of the coordination of alkali metal ions with the N atoms of the arylamine antioxidants are not clear. A great deal of work is still required to test this hypothesis. A major drawback to defining more rigorously the inhibition mechanism governing the activity of alkali metal salts has been the extreme difficulty in separating and identifying the intermediate oxidation reaction products, which are usually short-lived and present in extremely low concentrations. Gas chromatography and mass spectroscopy are among the tools being considered to resolve this problem.

5. Conclusions

In the isothermal DSC oxidation test, sodium stearate is an effective antioxidation synergist for DODPA in the ester lubricant. When combined with PANA and DODPA, sodium stearate can effectively reduce the increases in viscosity and acid number of the ester oil in the oxidation–corrosion test. Sodium stearate can reduce the free radical contents in the oxidized ester with arylamine antioxidants present.

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