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Evaluation of alkali metal salts as deposit inhibitors for synthetic lubricants by differential scanning calorimetry (DSC)

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Abstract

Differential scanning calorimetry (DSC) has been used to evaluate the deposit-forming tendencies of ester lubricants containing alkali salts. In the temperature programmed oxidation test, sodium acetylacetonate (NaA), sodium perfluorobutyrate (NaPFB), potassium trifluoroacetylacetonate (KTFA), and sodium trifluoroacetylacetonate (NaTFA) are not only good antioxidation synergists for arylamine compounds such as p,p'-dioctyldiphenylamine (DODPA), but also effective deposit inhibitors. When combined with arylamine antioxidants, the salts can also effectively reduce the increases in viscosity, acid number and deposit formation of the ester oils in oxidation–corrosion tests. © 1997 Elsevier Science B.V.

Keywords: Antioxidant; Deposit inhibitor; DSC; Alkali metal salt; Synthetic lubricant

1. Introduction

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. The oxidation and combustion of the esters often result in the formation of insoluble deposits. Thin oil films and hot spots in the oil–air system of an aero engine are mainly responsible for the deposit formation. Polymeric deposits may block oil jets and breather lines, clog filters and obstruct heat exchange. Zeman [1,2] and Zhang et al. [3,4] have reported on the usefulness of differential scanning calorimetry (DSC) in studying the thermal-oxidative degradation of lubricants and related problems including lubricant deposition phenomena.

Alkali metal salts are known to inhibit high temperature oxidation of the ester oils containing arylamine antioxidants such as N-phenyl-α-naphthylamine (PANA) and p,p'-dioctyldiphenylamine (DODPA) [5–8]. However, the effect of the salts on deposit-forming tendencies of the oils has not been reported. In this paper, temperature programmed DSC and an oxidation–corrosion test were employed to evaluate the performance of synergistic alkali metal salt-arylamine antioxidant systems in a pentaerythritol ester.

2. DSC technique and the two-peak method

The two-peak method to evaluate lubricants' deposit-forming tendency by DSC has been described by Zhang et al. [3].

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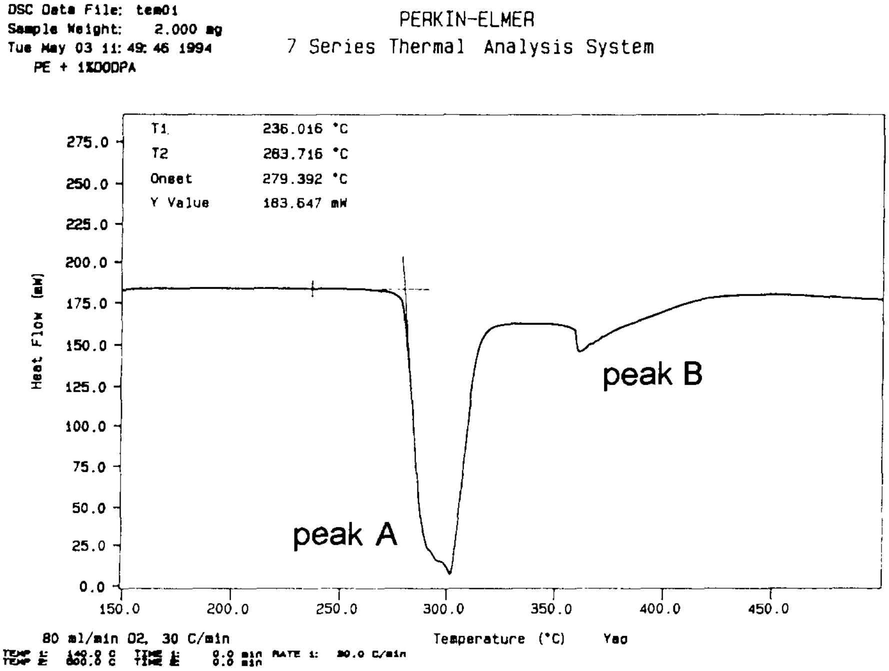

Fig. 1. DSC signal of the oxidation of the ester in the presence of DODPA.

Basically, the DSC technique measures the net heat evolved as a result of exothermic and endothermic reactions occurring in the sample as it is heated under controlled environmental conditions. A typical DSC thermogram for an oil subjected to a programmed temperature treatment is shown in Fig. 1. Two distinct exothermal peaks are seen under the conditions of the test. The first peak is referred to as Peak A and the second one, Peak B. Peak A is the primary oxidation peak, from which the incipient oxidation temperature (IOT) may be determined. The net heat represented by this peak reflects mainly oxidation reactions (exothermic).

Peak B, which appears at a higher temperature is attributed to the combustion of residual high molecular weight materials where the deposit is formed during the primary oxidation process, and it therefore provides a quantitative measurement of the deposit actually formed by a specific oil in a specific oxidation environment. However, different oils may have different evaporation characteristics. The oils which volatilized easily may loss a significant fraction of the sample before oxidation and polymerization process is complete. It thereby generates only a small amount of residue. As a result, a direct comparison using the area of Peak B may not be valid. A valid comparison among oils requests an appropriate normalization for Peak B to account for the absolute quantity of oils which are oxidized and contribute to the deposit formation. Ideally, the actual weight of the oil that goes through the oxidation and polymerization to form the deposit is the best normalization factor if it can be accurately measured. In practice, a direct measurement of the weight of the oil that actually contributes to the formation of deposit is difficult, since oil evaporation occurs simultaneously with oxidation and polymerization. Therefore, an indirect measurement is used. In a DSC thermogram, since Peak A is directly related to the actual amount of oil that goes through the primary oxidation and contributes to the formation of deposit, the area of Peak A may become an alternative normalization factor. In the study, the ratio of the area of Peak B to Peak A, denoted as B/A, can be used as the index for the deposit-forming tendency of an oil. A larger DSC B/A value means more deposit. Since the measurement of this index requires evaluation of both Peaks A and B, the method has been called the Two-Peak Method [3,4].

3. Experimental

3.1. Test basestock and additives

The base fluid used in testing the antioxidants was a pentaerythritol ester of a mixture of C_5–C_6 fatty acids, which was commercially available. Antioxidants such as *N*-phenyl-α-naphthylamine (PANA), *p,p'*-dioctyldiphenylamine (DODPA), metal deactivator benzotriazole (BTA) and were purchased from commercial sources. Sodium acetylacetonate (NaA), sodium perfluorobutyrate (NaPFB), potassium trifluoroacetylacetonate (KTFA), and sodium trifluoroacetylacetonate (NaTFA) were synthesized in the author' laboratory. All the additives were of more than 98% purity.

3.2. 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 a 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 temperature programmed mode where the incipient oxidation temperature (IOT) was measured. A higher incipient oxidation temperature (IOT) is indicative of improved oxidation stability.

The sample weight used was 2.00 mg (±0.05 mg), heating rate was 30 K min^{-1}. Ultra-pure oxygen was used. The oxygen flow rate was 80 cm^3/min. The incipient oxidation temperature (IOT) were obtained from the temperature programmed experiments by extrapolation of the front edge of the exothermic peak to the baseline.

3.3. 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 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ through 250 cm^3 of test oil in the presence of six metal coupons (Fe, Ag, Al, Mg, Cu, Ti) and determining the changes in metal weight the

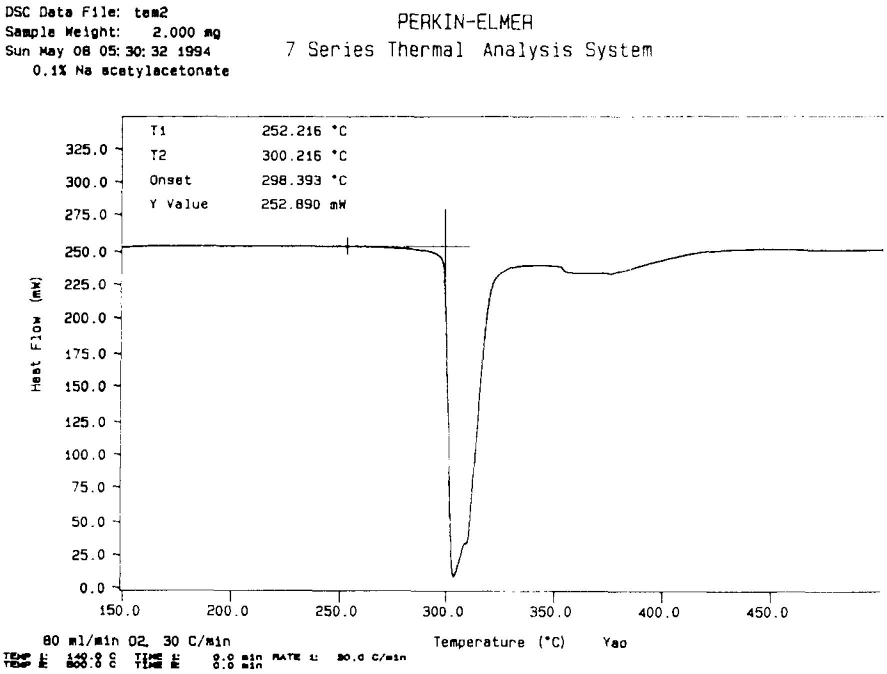

Fig. 2. DSC signal of the oxidation of the ester in the presence of DODPA and NaA.

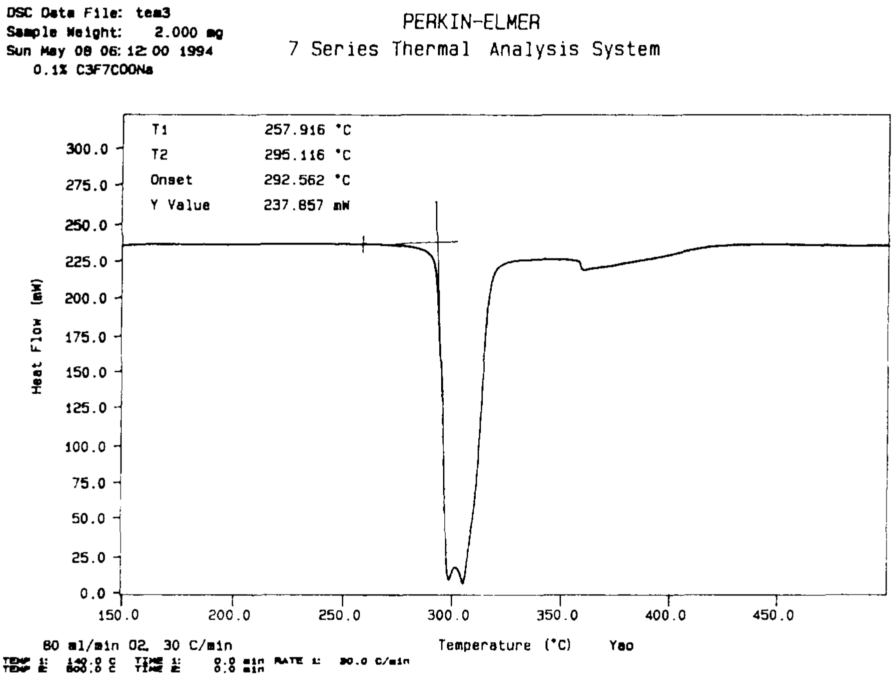

Fig. 3. DSC signal of the oxidation of the ester in the presence of DODPA and NaPFB.

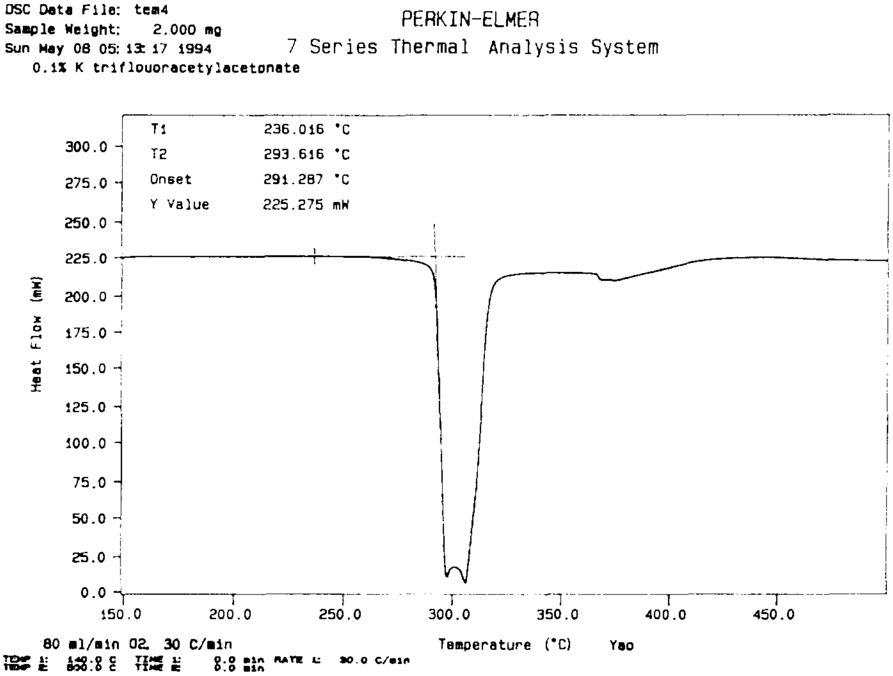

Fig. 4. DSC signal of the oxidation of the ester in the presence of DODPA and KTFA.

viscosity and acid number of the oil and observing the deposit produced in the oil.

4. Results

NaA, NaPFB, KTFA and NaTFA were added separately at 0.1% concentration to the ester basestock containing 1% DODPA, and the inhibited fluids were evaluated by temperature programmed DSC at 30 K min^{-1}. The results are shown in Figs. 1–5 which demonstrate the exothermic thermal-oxidative degradation of the esters without and with the alkali metal salts and the determination of IOTs. Thus, 1% DODPA provided a IOT of 279°C, but the combinations of 1% DODPA with 0.1% NaA, NaPFB, KTFA and NaTFA gave IOTs of 298.39°C, 292.56°C, 291.28°C and 286.19°C. Although alkali metal salt alone posses no antioxidation activity for ester lubricants [5,6], they can enhance the effectiveness of arylamine antioxidants. Similar results have been reported with isothermal DSC oxidation tests [7,8].

The deposit-forming tendencies of the five oils and the base ester by DSC two-peak method are listed in Table 1. One can find from Table 1 that, DODPA almost did not have any influence on the deposit formation of the ester. But all of the four alkali metal salts were effective deposit inhibitors.

Table 1
DSC peak areas and B/A ratio (base formulation – Ester: 99.0, DODPA: 1.0)

Alkali metal salt, mass%	IOT C	Peak A area mJ	Peak B area mJ	B/A ratio
Ester[a]	236.10	6768.8	592.6	8.75
None	279.39	7734.6	674.8	8.72
NaA, 0.1	298.39	6672.0	231.0	3.46
NaPFB, 0.1	292.56	7871.8	195.0	2.48
KTFA, 0.1	291.28	7788.1	79.8	1.02
NaTFA, 0.1	286.19	7812.0	124.2	1.59

[a] Without DOPDA.

The effectiveness of the alkali metal salts as deposit inhibitors and synergistic antioxidants to PANA and DODPA was also demonstrated in the oxidation-corrosion test. Data are shown in Table 2. In Table 2 we can see that the uses of 0.06% of the alkali metal salts substantially reduced the increases in viscosity and acid number and the deposit formation. The changes

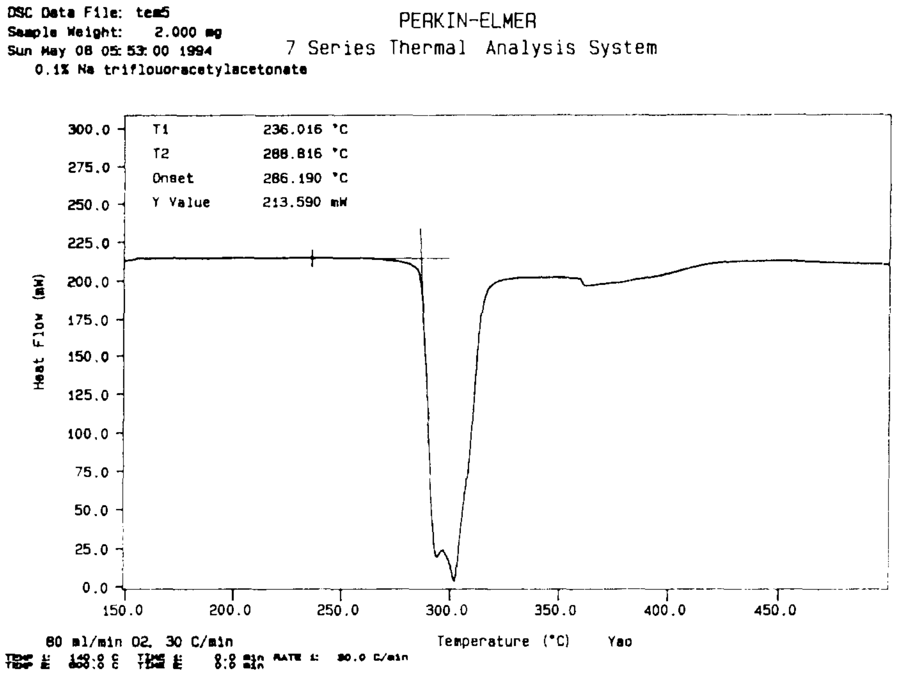

Fig. 5. DSC signal of the oxidation of the ester in the presence of DODPA and NaTFA.

Table 2
240°C Oxidation–corrosion test results[a] (effect of the alkali metal salts; base formulation – Ester: 97.90, PANA: 1.00, DODPA: 1.00, BTA: 0.10)

Alkali metal salt, mass%	Viscosity increase 40°C%	Acid no. increase	Deposits
None	34.0	4.11	Medium coke, heavy sludge
NaA, 0.1	14.8	1.20	Light coke, very light sludge
NaPFB, 0.1	17.8	0.90	Light coke, no sludge
KTFA, 0.1	19.8	1.15	No coke, no sludge
NaTFA, 0.1	21.8	1.67	No coke, no sludge

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

in metal weight are not reported in Table 2 due to no obvious metal corrosion both with and without the alkali metal salts in the oils.

5. Conclusions

1. In the temperature programmed DSC oxidation test, NaA, NaPFB, KTFA and NaTFA are effective antioxidation synergists for DODPA in the ester lubricants.
2. In the temperature programmed DSC oxidation test, NaA, NaPFB, KTFA and NaTFA are effective deposit inhibitors for the ester lubricants containing DODPA.
3. When combining with PANA and DODPA, NaA, NaPFB, KTFA and NaTFA can effectively reduce the increases in viscosity and acid number of the ester oil and deposit formation in the oxidation–corrosion test.

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