Journal of Thermal Analysis, Vol. 32 (1987) 1805–1808

INVESTIGATION OF THERMOOXIDATIVE STABILITY OF OILS BY THERMAL ANALYSIS METHODS

M. Paczuski and *K. Kardasz*

INSTITUTE OF CHEMISTRY, WARSAW TECHNICAL UNIVERSITY,
BRANCH IN PŁOCK, ŁUKASIEWICZA 17, 09–400 PŁOCK, POLAND

Two base oils, obtained on a laboratory scale, were investigated with a derivatograph and by means of DSC. The sensitivities of the oils to some antioxidants were also examined. The high thermooxidative stability of the oil obtained from a preoxidized atmospheric crude residue was confirmed.

Thermal analysis methods are applied for the investigation of the physico-chemical properties of base stocks and their compositions with additives. Series of oil quality parameters, such as specific heat, solubility in normal paraffins, freezing point, boiling point, and oxidation and destruction temperatures are characterized by TA methods.

The effectiveness of inhibitors and the oxidative stability are often estimated via these techniques.

The oxidative or thermooxidative stability is characterized by two parameters, the oxidation beginning temperature (OBT) and the heat value connected with this process. The leading inhibitor in the base oil causes an increase of the OBT, and the magnitude of the OBT is a measure of the effectiveness of the oxidation inhibitor.

The investigation of oil oxidation stability by mass decrement comparison under isothermal conditions allows determination of the induction period and the influence of the inhibitor.

Because of the precision, the short time and the small amounts of samples, thermal methods are utilized to investigate new efficacious oxidation inhibitors. Tests are made, for example, of the influence of the metal and the alkyl substituent in salts of dithiophosphoric acid esters (DTPE) [1–4].

Comparison of the thermal and oxidative stabilities of mineral oils in inert gas and oxidative environments also allows quality estimations on used oils.

The present paper describes the oxidative stability and sensitivity to some typical inhibitors in relation to two different base stocks.

The two base oils were obtained from the vacuum fractions (350–425° boiling

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

range) from an atmospheric crude residue (RU) and an oxidized residue (RO), after selective furfural refining, dewaxing with a solvent mixture and complementary refining with decoloured clay. Mild oxidation of the atmospheric crude residue leads to complex chemical free radical reactions, causing different structural-group compositions of the distillates. A higher output of good-quality base oil is obtained after preliminary oxidation of the atmospheric residue.

Investigations were performed with a Q-derivatograph. Oil samples were heated in air up to 600°, at a rate of 10 deg/min, using alumina as a matrix. The temperatures of 5, 10 and 50% mass decrements were compared to characterize the thermooxidative stability of the oil (Fig. 1).

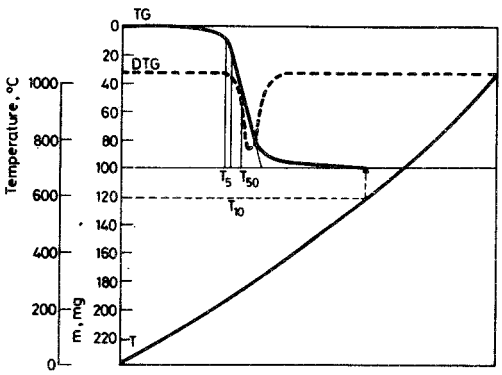

Fig. 1 Thermal curves of oil

The analysed base oils were denoted BU, oil from unoxidized raw material, and BO, base oil obtained by the modified method. The results of thermal analysis are given in Table 1.

A comparison of the characteristic temperatures in this investigation indicates the higher stability of the base oil produced from the oxidized residue.

The corresponding characteristics of two base stock compositions with the selected inhibitors Jonol (2,6-di-tert-butyl-p-cresol) and Acorox 88 (zinc salt of

Table 1 Characteristic parameters of thermooxidative stability of base oils

Mass decrement, %	Temperature, °C	
	BU	BO
5	250	252
10	300	300
50	343	372

Table 2 Characteristic parameters of thermooxidative stability of base oil—inhibitor mixtures

Mass decrement, %	Temperature, °C			
	BU+J	BU+A	BO+J	BO+A
5	260	252	257	270
10	300	302	300	300
50	360	350	350	370

dithiophosphoric acid alkyl ester) were determined. Jonol was added in a quantity of 0.1% by mass, and Acorox in 0.6% (Table 2).

Inhibitor addition elevated the temperature of 5% mass decrement for all compositions. There was a higher sensitivity to Jonol (Δt_5 = 10 degrees) for the classical technology base oil than for the base oil from the preliminary oxidized residue (Δt_5 = 5 degrees). The multifunctional additive Acorox gave a higher sensitivity with BO (Δt_5 = 18 degrees) than with BU (Δt_5 = 2 degrees). The best mixture seems to be the composition BO+Acorox.

The resistance of oils to oxidation can be estimated from the Conradson coke number, which correlates well with the thermal analysis residue at 600°. Comparison of the coke residues at 600° for these oils indicated the higher stability of BO (1.2% mass) than that of BU (1.7% mass). The BO and BU compositions with the inhibitors exhibited similar relations.

The results of DSC measurements are demonstrated in Figs 2 and 3. These confirm the results obtained with the derivatograph.

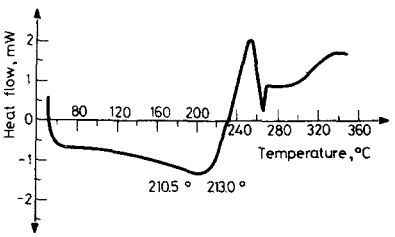

Fig. 2 DSC curve of oil BO+A. Sample size: 3 mg. Heating rate: 10 deg/min

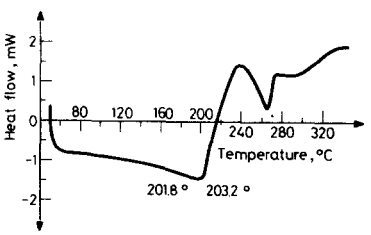

Fig. 3 DSC curve of oil BU+A. Sample size: 31 mg. Heating rate: 10 deg/min

The distinct difference between the onset temperatures proves the higher oxidative stability of BO than that of BU.

The differences in the physico-chemical properties of these base oils follow from the group compositions and the paraffinic, naphthenic and aromatic hydrocarbon structures. The resistance of the oils to oxidation is connected mainly with the chemical compositions and capacities of the resins. They can play the role of natural inhibitors.

The explanation of the better thermooxidative stability and the higher sensitivity to inhibitors (observed in the TA investigations) of the base oil obtained from the mild oxidized residue requires detailed investigations of its chemical composition and mechanism of interaction with additives.

* * *

The authors are grateful to the Institute of Petroleum Technology for the DSC measurements.

References

1 N. A. Neczitajło, Neftechimija, 18 (1978) 827.
2 I. M. Tiunowa and K. M. Babysztowa, Chimia i techn. topliw i masieł, 5 (1982) 35.
3 D. E. Diskina and I. M. Tiunowa, Neftepiererabotka i neftechimia, 2 (1978) 12.
4 G. A. Trofimow and J. S. Zasławskij, Neftepiererabotka i neftechimia, 1 (1978) 19.

Zusammenfassung — Zwei im Labormaßstab hergestellte Rohöle wurden mit einem Derivatographen und mittels DSC untersucht. Die Empfindlichkeit der Öle gegenüber Antioxidanten wurde ebenfalls geprüft. Es wurde eine hohe thermooxidative Stabilität des aus einem präoxidierten atmosphärischen Rohstoffrestes erhaltenen Öls nachgewiesen.

Резюме — С помощью дериватографа и дифференциальной сканирующей калориметрии изучены две основы масел, полученных в лабораторных условиях. Исследована также их чувствительность к некоторым антиокислителям. Подтверждена высокая стойкость к термоокислению масла, полученного из предварительно окисленного остатка сырой нефти.