Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 435 (2005) 172–175

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of thermo-oxidative characteristics of gear oils by different techniques: Effect of antioxidant chemistry

Mukul R. Jain*, R. Sawant, R.D.A. Paulmer, D. Ganguli, G. Vasudev

Bharat Petroleum Corporation Limited, Research and Development Centre, Mumbai 400015, India

Received 23 December 2004; received in revised form 4 May 2005; accepted 17 May 2005
Available online 27 June 2005

Abstract

This paper deals with determination of the oxidation stability of gear oils formulated with antioxidants of different chemistries. The oxidation stability has been studied by PDSC, TGA, micro-oxidation, RPVOT and IP 48. The effect of different antioxidants on the thermo-oxidative properties of gear oil is evaluated.

Keywords: Gear oil; Antioxidants; Lubricants; Thermo-oxidative stability

1. Introduction

Development of gear oil for any system is a lengthy and complicated process. Some of the key steps in the process are selection of a base stock, evaluation of additives and formulation of the oil with best trade-off in performance and cost [1]. Gear oils are broadly classified into three types: rust and oxidation inhibited, compounded and EP gear oils [2]. However, better oxidation stability is a major requirement for all the types as this is one property that decides the service life of the lubricant [3]. Oils lacking this, thicken by oxidation and deteriorate rapidly. Sludge and deposits form, clogging oil passages, altering heat transfer rates, depleting additive and corroding the gears [4]. Oils with poor thermal/oxidative stability have a short useful life and tend to shorten the life of the equipment they lubricate [5].

The thermo-oxidative degradation of gear oils is similar to that of other lubricating oils [6]. The oil undergoes two-step degradation process [7]. In the primary step, hydrocarbon molecules in the oil are cleaved thermally forming organic radicals, these radicals react with oxygen, which leads to the formation of further radicals, such as peroxy radicals, as well as peroxides [8]. Antioxidants stabilize gear oils against oxidation [9]. The antioxidants trap the active radical species, primary antioxidants are used for this purpose, or decompose the peroxides by secondary antioxidants. The primary degradation may also lead to volatile compounds. In the secondary step oligomers are formed leading to formation of sludge and deposits. It is important to determine the effectiveness of these antioxidants and to establish effectiveness in the presence of other additives in the oil. Lubricant manufacturers use a variety of chemical and physical laboratory bench tests. In the present work gear oils with different antioxidant chemistries have been formulated and the effectiveness of these antioxidants studied by different techniques.

2. Experimental

The blends used for study were prepared in Group II base oil with the same additive package of antiwear agent, defoamer, demulsifier, rust and corrosion inhibitor. The blend details are shown in Table 1. Blends were tested for different properties by standard test methods [10]. The thermo-oxidative properties were determined with high pressure differential scanning calorimetry (PDSC),

---

* Corresponding author. Tel.: +91 2224176367; fax: +91 2224176367.
E-mail addresses: jainmukul@bharatpetroleum.com, drmukuljain@indiatimes.com (M.R. Jain).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.05.016

Table 1
Blend details of gear oil prepared

Blend[a]	Antioxidant type
AO I	Nil
AO II	Irganox L 57 (aminic)
AO III	Irganox L 135 (phenolic)
AO IV	Irganox L 57 (aminic) + Irganox L 135 (phenolic)

[a] Commercially available additive package consisting of antiwear agent, defoamer, demulsifier and corrosion inhibitor were used in all formulations.

thermogravimetric analysis (TGA), micro-oxidation, rotating pressure vessel oxidation test (RPVOT) and IP 48.

PDSC applications are run either in an isothermal or a programmed temperature mode. A number of modifications of the method are in use including sample size, flow rates, temperature sequence and type of sample pan. The samples were run on a Q 1000, PDSC, TA instruments, USA.

TGA is useful in comparing the volatility of lubricants under thermal and oxidative conditions. Earlier studies used TGA to evaluate both base stocks and additives [11]. In the present study thermograms were recorded on a Q50, TGA, TA Instruments, USA.

RPVOT is used to evaluate the oxidation stability of new and in-service lubricating oils in the presence of water and a copper catalyst coil at a predetermined temperature and oxygen pressure. Tests were carried out on Koehler (Germany) equipment in accordance to ASTM D 2272 [12].

IP 48/97 indicates the tendency of lubricating oil to deteriorate on oxidation under specified conditions. A measure of the deterioration is obtained by comparison of the viscosity, carbon residue and acid number before and after the test. The tests were carried out on Petrotest (USA) equipment in accordance to IP 48 [13].

The micro-oxidation test determines oxidative behavior of oils while simulating thin film conditions. The test method conforms to ASTM Draft Method and measures oil volatility and oxidative evaporation loss [14]. The tests were carried out on Koehler (Germany) equipment.

3. Results and discussion

The test results on the gear oil blends are tabulated in Table 2. The thermo-oxidative property as evaluated by different methods is shown graphically in Figs. 1–4.

Fig. 1 shows the PDSC curves for the different gear oil blends in standard copper pans. Initially a sample was evaluated at a programmed temperature rate of 10 °C/min using 2 ± 0.25 mg of sample under 896.3 kPa of oxygen. Based on the result of this test, an isothermal temperature of 160 °C was selected for the isothermal evaluations. The oxidation induction time (OIT) for all the blends is shown in the same figure. The oxidation induction time is determined in the same way as reported by Rhee [15]. The OIT values are in the order AO II > AO IV > AO III > AO I. Synergism of antioxidants is not contributing much to delay the oxidation process. The copper pan acts as catalyst to induce faster oxidation, as the same was not found in the case of OIT determination in aluminum pans.

The RPVOT results are shown in Fig. 2. The RPVOT values are in the order AO II > AO IV > AO III > AO I. This agrees with the performance observed by PDSC. In the IP 48 method the test sample is subjected to a severe oxidation condition by heating to 200 °C and passing air through it at a rate of 15 l/h for two periods of 6 h with a gap of about 15–18 h between them. After standing for 15–30 h, the kinematic viscosity, carbon residue and total acid number (TAN) of the oxidized oil are determined and compared with those from corresponding tests on the unoxidized oil. The results are shown in Fig. 3. The increase in viscosity is an indication of the formation of oligomers due to oxidation. The viscosity ratio values show the least increase in viscosity for blend AO II and maximum for AO I. This indicates AO I has the least thermo-oxidative-stability and maximum for AO II. The percent evaporation loss values are in the same order. This agrees with the results observed by the other methods. However, the TAN value for AO IV is the least. The formation of oligomers and not acid at the end of the oxidation may be responsible for low values of TAN for AO IV [16].

Table 2
Physicochemical and other properties of blends prepared – IS 8406: 1993

Sr. no.	Characteristics	Requirements	AO I	AO II	AO III	AO IV
1	Kinematic viscosity at 40 °C (cSt)	414–506	468.9	468.1	467.8	466.7
2	Flash point COC, Min (°C)	230	270	266	275	268
3	Viscosity index, Min	90	94	91	91	94
4	Pour point, Max (°C)	0	−3	−3	−6	−6
5	Acidity, inorganic	Nil	1.123	1.167	1.257	1.328
6	Cu strip corrosion at 100 ± 1 °C for 3 h	Not worse than 1	1a	1a	1a	1a
7	Rust protection	No rust after 24 h with synthetic sea water	Pass	Pass	Pass	Pass
8	Ash, % by mass, Max	0.1	Traces	Traces	Traces	Traces
9	Timken EP test OK load, Min (kg)	27	Pass	Pass	Pass	Pass
10	Four ball EP test					
	(a) Weld load, Min (kg)	250	315	315	315	315
	(b) LWI, Min (kg)	45	Pass	Pass	Pass	Pass
11	Four ball wear, scar dia, Max (mm)	0.35	Pass	Pass	Pass	Pass
12	FZG Niemann EP test, pass, Min	11 load stage	12th	12th	12th	12th

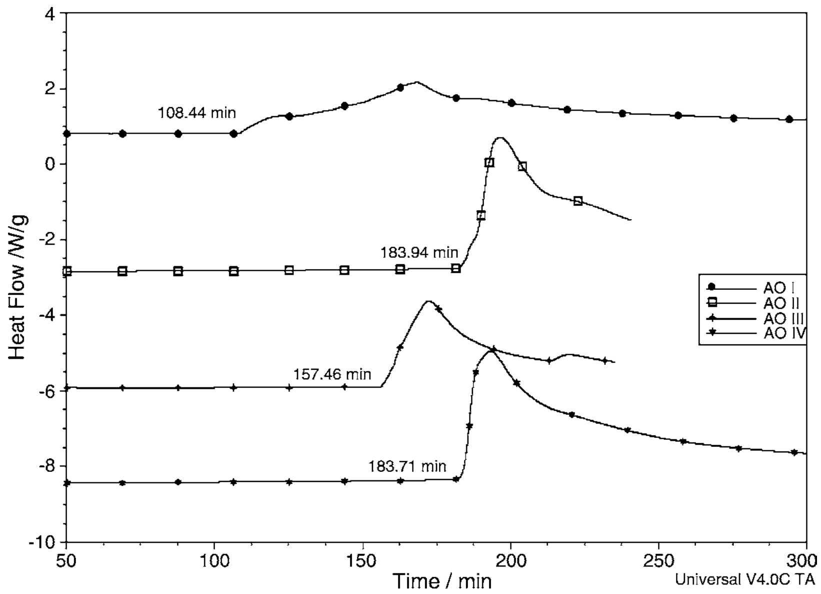

Fig. 1. Isotherms of 160 °C and 896.3 kPa of blends AO I, AO II, AO III and AO IV.

Fig. 4 shows the results obtained by micro-oxidation test. In this method a small quantity of oil (40 μl) is maintained at 225 °C for 2 h and exposed to airflow at 20 ml/min. The percent-oxidized at the end of the test is measured. The thermo-oxidative stability for the blends is in the order AO II > AO IV > AO III > AO I. This is in agreement with the results as obtained by other methods.

In TGA, 2 mg of sample was heated at 20 °C/min in an inert pan under gas flow of 10 ml/min of inert atmosphere or oxygen. The thermograms for two blends are shown in Fig. 5. The thermo-oxidative stability of AO II is better than that of AO I. This again indicates better antioxidant effectiveness in blend AO II.

As observed by all the techniques, the aminic antioxidant gave better thermo-oxidative stability than the phenolic

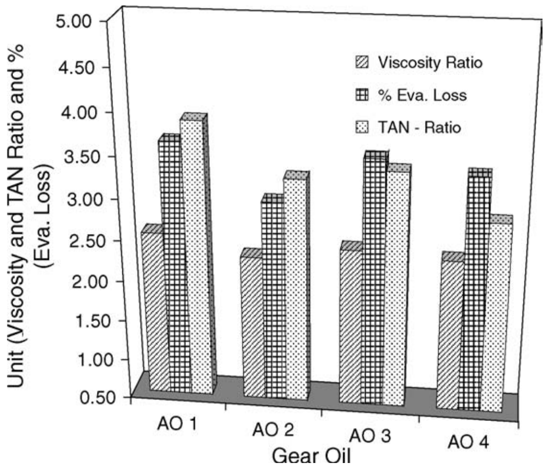

Fig. 3. IP 48 results for blends AO I, AO II, AO III and AO IV.

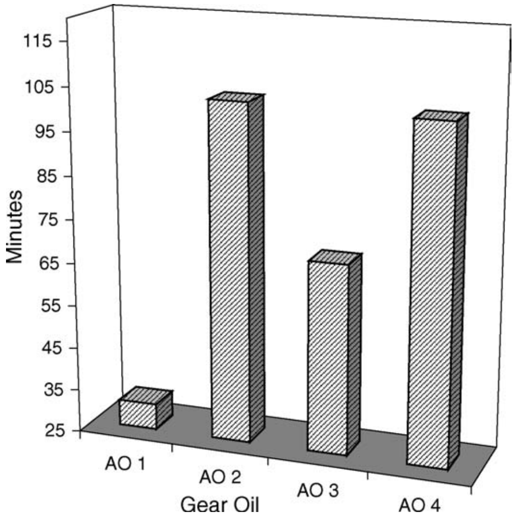

Fig. 2. RPVOT results for blends AO I, AO II, AO III and AO IV.

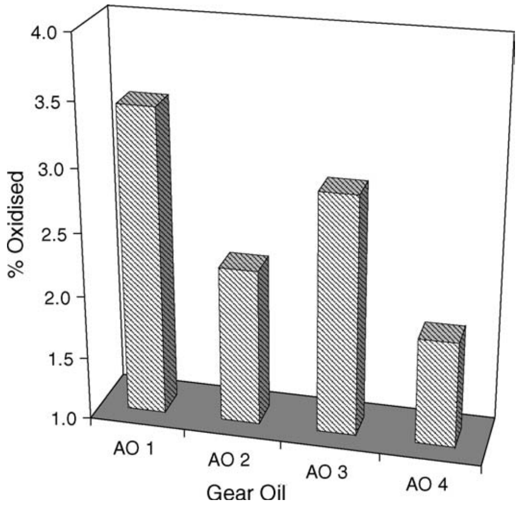

Fig. 4. Micro-oxidation results for blends AO I, AO II, AO III and AO IV.

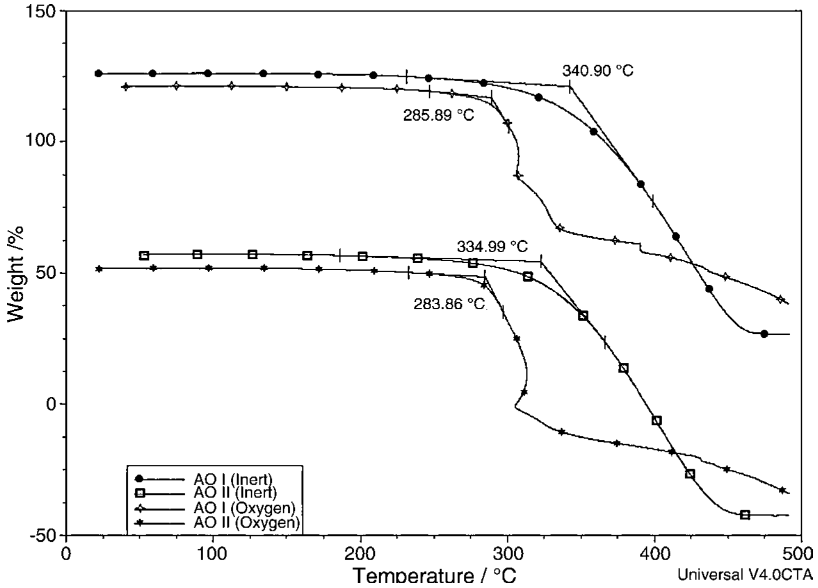

Fig. 5. TGA of blends AO I, AO II, AO III and AO IV.

antioxidant. The reason for this can be attributed to the fact that aminic antioxidants react in a catalytic manner at the test chosen temperature [8]. They are regenerated during a certain number of cycles, actively participating as radical scavengers and breaking chain reactions. They usually react with 30–60 radicals per aminic antioxidants molecule, before being consumed [17]. Phenolic antioxidants act in a similar manner but they react only stoichiometrically, that is with 2–4 radicals [8,18]. This may be the reason for the poor thermo-oxidative stability for blend AO III, in comparison to blend AO II. The experimental work also establishes the synergistic effect obtained by using a combination of aminic and phenolic antioxidants where each antioxidant working in a different temperature range.

The results establish a positive correlation between the various tests and confirm the use of analytical tools like PDSC as effective and rapid tools for determining thermo-oxidative stability. The older techniques are more time consuming and require a larger sample.

References

[1] G.P. Andrew, Lubr. Eng. 44 (1988) 210–222.

[2] H.S. Cheng, in: B. Bhushan (Ed.), Modern Tribology Handbook, vol. II, CRC Press, New York, 2001, pp. 1095–1129.

[3] A.G. Papay, D.W. Dinsmore, Lubr. Eng. 32 (1976) 229–234.

[4] R.L. Errichello, in: E.R. Booser (Ed.), Tribology Data Handbook, CRC Press, New York, 1997, pp. 781–799.

[5] C.A. Midgal, in: L.R. Rudnick (Ed.), Antioxidants in Lubricants Additive Chemistry and Applications, Marcel Dekker Inc., New York, 2003, pp. 1–27.

[6] P. Rohrbach, P.C. Hamblin, Lubr. Sci. 14 (1) (2001) 3–23.

[7] D. Chasan, Oxidation Inhibition in Organic Materials, CRC Press, New York, 1990.

[8] M. Rasberger, in: R.M. Mortier, S.T. Orzulik (Eds.), Chemistry and Technology of Lubricants, VCH Publishers Inc., New York, 1992, pp. 83–134.

[9] R.K. Jensen, M.D. Johnson, S. Korcek, M. Zinbo, Ind. Eng. Chem. Prod. Res. Dev. 25 (4) (1986) 621–27.

[10] Gear Lubricants for Enclosed Industrial Gear Drives – Specification, Indian Standard, IS 8406, 1993.

[11] S.M. Hsu, A.L. Cummings, D.B. Clark, SAE Technical Paper No. 821252, 1952.

[12] Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel (RPVOT), ASTM International, USA, ASTM D 2272 – 98.

[13] Determination of Oxidation Characteristics of Lubricating Oil, The Institute of Petroleum, London, IP 48.

[14] Micro-Oxidation Test, ASTM Draft Method, Operation and Technical Manual, Koehler Instrument Company.

[15] I.S. Rhee, NLGI Spokesman 55 (1991) 7-123–16-132.

[16] J.M. Perez, Thermochem. Acta 357/358 (2000) 47–56.

[17] H. Berger, T.A. Bolsman, D.M. Brouwer, in: G. Scott (Ed.), Development in Polymer Stabilization, vol. 6, Applied Science Publishers, London, 1983, pp. 1–27.

[18] J.L. Reyes-Gavilan, P. Odorisio, A review of the mechanism of action of antioxidants, metal deactivators and corrosion inhibitors, in: NLGI Conference, May 2002.