Study on the oxidative stability of poly α-olefin aviation lubricating base oil using PDSC method

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Abstract. The oxidation stability of the domestic and import PAO aviation lubricating base oil was studied by the method of pressurized differential scanning calorimetry testing the initial oxidation temperature. The effects of anti-oxidants were investigated, and the best ratio of antioxidants was determined.

1. Introduction
Poly-α-olefin (PAO) aviation lubricating oil has many high performances, such as good viscosity-temperature performance, low pour point, high flash point, low temperature fluidity, wide operating temperature range, high hydrolysis resistance, and good compatibility with petroleum refining base oil[1,2]. It can ensure the mechanical device playing excellent performance in harsh environment. During engine operation, the temperature of aviation lubricating oil in the tank will be up to 160°C, while the temperature will be higher between the friction disks. In high-temperature environment, the decay of the lubricating oil will lead to the viscosity-rising, the acid value-increasing, sediment and deposit in contact with air and under the catalytic action of copper, iron and other metals[3]. Eventually the lubricating oil will become invalid, which will affect the performance of aircraft engines, make the shaft-braking and other catastrophic failure [4,5]. Therefore, oxidation stability is an important index of lubricating oil quality, which directly affecting the performance of lubricating oil and determining the service life.

Methods to evaluate the oxidation stability of lube oil are various, such as rotary oxygen bomb test, openings in vitro oxidation test, etc. Most of these methods have the disadvantages of large amount of samples, operating complicated, measuring a long time, poor reproducibility and other shortcomings. Early differential scanning calorimetry (DSC) simulates the oxidation process under boundary lubrication conditions. But the method will cause great error analysis, due to the large number of lubricating oil evaporation and absorb heat under the condition of high temperature [7-10]. In recent years, high-pressure differential scanning calorimetry (PDSC) analysis develops on the basis of the
DSC, which is a very effective method to evaluate the oxidation stability of lubricating oil, overcoming the shortcoming of DSC with trace, rapid, accurate and other advantages [11].

In this paper, PDSC is used to investigate the oxidation stability of domestic and imported poly-$\alpha$-olefin aviation lubricants, as well as examine both lubricating base oil sensitivity of three commonly used antioxidants.

2. Experimental

2.1. The main materials and equipment
The lubricating oil used in the experiment is from Shanghai FOX Chemical Technology Company and an oil research institute. The physical and chemical properties of the two base oils are shown in Table 1. The three antioxidants used in the experiment are shown in Table 2. The PDSC is PDSC8000 produced by Shanghai Perkin Elmer.

| Test Item                        | Domestic PAO | Import PAO | Test Method |
|----------------------------------|--------------|------------|-------------|
| Kinematic Viscosity (40°C) (mm² s⁻¹) | 17.91        | 17.94      | GB/T 265    |
| Kinematic Viscosity (100°C) (mm² s⁻¹) | 4.817        | 4.018      | GB/T 265    |
| Viscosity Index                  | 121          | 131        | GB/T 1995   |
| Flash Point (COC) (°C)            | 214          | 201        | GB/T 3536   |
| Pour Point (°C)                   | -62          | -68        | GB/T 3535   |
| Acid Number (mg KOH g⁻¹)         | 0.01         | 0.009      | GB/T 7304   |

Table 2. The antioxidants used in the experiments

| Item                          | Type              | Formula |
|-------------------------------|-------------------|---------|
| 2,6-diisopropyl-4-methylphenol (T501) | Phenolic antioxidant | ![image] |
| Bis (4-‘Ctylphenyl ) amine (Tz516) | Amine antioxidant | ![image] |
| N-phenylnaphthalen-1-amine (T531) | Amine antioxidant | ![image] |

2.2. Experimental methods
Using the programmed temperature method, the oil is heated gently in a certain pressure of oxygen atmosphere. And the initial oxidation temperature (IOT) is measured to characterize oxidation stability.
of the sample. The higher the initial oxidation temperature is, the better the oxidation stability. Experimental measurement conditions: temperature rise rate is 10 °C/min, oxygen pressure is 1.0-1.5MPa, oxygen flow rate is 100mL/min, 6mm opening aluminum pan, dosage of samples is 3 μg.

3. Results and discussion

3.1. Comparison of oxidation stability of two aviation lube base oil

The initial oxidation temperature of domestic and imported PAO aviation lubricating oil was shown in table 3.

| Item       | IOT (°C) | FOT (°C) | Enthalpy (J g⁻¹) |
|------------|----------|----------|------------------|
| domestic PAO4 | 202.79   | 218.80   | -2572.83         |
| imported PAO4 | 205.99   | 226.61   | -3275.96         |

The oxidation of base oil is an exothermic reaction. When the oil is heated in the oxygen air, there will be an obvious peak in the PDSC curve as soon as the base oil begins to oxidize, and the rate of heat release and is corresponding to the speed of oxidation reaction. The initial oxidation temperature of base oil and the fastest oxidation temperature are lower, that the oil oxidation stability is poor. It can be seen from Table 3, the domestic PAO began to oxidation at 202 °C, and reached maximum oxidation rate at 218 °C; while the imported PAO began to oxidation at 205 °C, and reached maximum oxidation rate at 226 °C. As a result, the oxidation stability of the domestic PAO is similar to the imported with a little difference.

3.2. Study on the susceptibility of two base oil to oxidant T501

Add the oxidant T501 into domestic and imported PAO of 0.5%, 1.0%, 1.5% and 2.0% by volume, comparing the susceptibility of two lubricating oil receptivity. The results were shown in Table 4.

| Antioxidant content (%) | IOT (°C) | Domestic PAO4 | Imported PAO4 |
|-------------------------|----------|---------------|---------------|
|                         |          |               |               |
| 0                       | 202.79   | 205.99        |               |
| 0.5                     | 206.47   | 207.83        |               |
| 1.0                     | 207.15   | 209.91        |               |
| 1.5                     | 208.58   | 210.21        |               |
| 2.0                     | 207.91   | 210.36        |               |

It can be seen from the table that the IOT of two kinds of PAO base oil with T501 increased slightly, and will gradually increase with the increase of the antioxidant content. But the upward trend is not obvious, the temperature changes all-around 5 °C, when the antioxidant content is more than 1.5%, the rise in temperature tends to be gentle.

3.3. Study on the susceptibility of two base oil to oxidant T531
Add the oxidant T531 into domestic and imported PAO of 0.5%, 1.0%, 1.5% and 2.0% by volume, comparing the susceptibility of two lubricating oil receptivity. The results were shown in Table 5.

**Table 5.** The IOT of two PAO aviation lubricating base oil added T531

| Antioxidant content (%) | IOT(℃) | Domestic PAO4 | Imported PAO4 |
|-------------------------|--------|---------------|---------------|
| 0                       | 202.79 | 205.99        |               |
| 0.5                     | 232.26 | 231.77        |               |
| 1.0                     | 236.76 | 236.83        |               |
| 1.5                     | 237.63 | 240.36        |               |
| 2.0                     | 241.19 | 240.28        |               |

It can be seen from the table that the IOT of two kinds of PAO base oil with T531 increased sharply, while the domestic PAO aviation lubricating oil increased nearly 39℃, and the imported PAO aviation lubricating oil increased nearly 35℃. The IOT of domestic PAO will be higher, when the antioxidant content is more, as well as the imported. But when the antioxidant content exceeds 1.5%, the IOT of the imported PAO changed little.

3.4. *Study on the susceptibility of two base oil to oxidant Tz516*

Add the oxidant Tz516 into domestic and imported PAO of 0.5%, 1.0%, 1.5% and 2.0% by volume, comparing the susceptibility of two lubricating oil receptivity. The results were shown in Table 6.

**Table 6.** The IOT of two PAO aviation lubricating base oil added Tz516

| Antioxidant content (%) | IOT(℃) | Domestic PAO4 | Imported PAO4 |
|-------------------------|--------|---------------|---------------|
| 0                       | 202.79 | 205.99        |               |
| 0.5                     | 228.97 | 230.87        |               |
| 1.0                     | 235.71 | 236.67        |               |
| 1.5                     | 247.53 | 246.05        |               |
| 2.0                     | 248.86 | 250.92        |               |

It can be seen from the table that the IOT of two kinds of PAO base oil with Tz516 increased sharply, while the domestic PAO aviation lubricating oil increased nearly 46℃, and the imported PAO aviation lubricating oil increased nearly 45℃. And the IOT of both two kinds of PAO will be higher, when the antioxidant content is more. But when the antioxidant content exceeds 1.5%, the rise in temperature tends to be gentle.

3.5. *Discussion*

Oxidation of the lubricating oil is a chain reaction of free radicals, while some acidic materials such as aliphatic acids, aldehydes and ketones will be produced in the reaction process, and they will catalyst the oxidation reaction of lubricants[12]. In terms of molecular structure, T531 and Tz516 are amine antioxidants, T501 is phenolic antioxidants. The mechanism of phenolic antioxidants is to react with
the free radical produced in the chain reaction, generating more stable chemical substances, thus interrupting the chain reaction, delaying the oxidation rate. While amine antioxidants will react with the acidic materials produced in the oxidation reactions, catalytic reduction of such compounds in the lubricating oil in the oxidation process, decreasing the oxidation reaction rate, improving the oxidation stability of the lubricating oil. The phenolic antioxidants are used in the relatively low temperature range, while the amine antioxidants are higher. The oxidation temperature of PAO usually reached to 200°C or more. As a result the IOT increased greatly, antioxidant performance significantly, when added the amine antioxidants.

4. Conclusion

It can be find from the results of PDSC that the domestic PAO began to oxidize at about 202°C, accelerated oxidation at 218°C; while imported PAO began to oxidize at about 206°C, accelerated oxidation at 227°C. Thus, the oxidation stability of domestic PAO aviation lubricating oil is slightly lower than the imported ones.

When adding an antioxidant, oxidation stability of domestic and imported PAO aviation lubricants enhanced, both trends are consistent, but different sensitivity to different antioxidant. The IOT of two base oil will increase slightly adding the antioxidants T501 and with increase of the antioxidant content, base oil of incipient oxidation temperature is gradually increased, but the upward trend was not obvious; when adding antioxidants T531 and Tz516, the initial oxidation temperature of two base oils have significantly increased, and with the increase of the antioxidant content, the initial oxidation temperature of the base oil to improve significantly, but when the antioxidant content is more than 1.5%, a rise in temperature tends to be gentle. Thus, the antioxidant property of amine antioxidant is better than phenolic antioxidants for PAO aviation lubricants.

It has been found that the oxidation stability of both domestic PAO and imported PAO were similar and the sensitivity of antioxidants are basically the same. Considering the oxidation stability of the base oil will not change significantly as long as the antioxidant content increase, the best antioxidant dose is 1.5%. So as to maximize play the antioxidant properties of antioxidant and can guarantee the economy.

To sum up, characterized by less sample, simple operation, high sensitivity, high accuracy and low cost, PDSC is widely used in the study of lubricating oil. It can be used to determinate the antioxidant properties of base oil and antioxidants, analyse the correlation between antioxidant activity and antioxidant content of lubricating oil, to calculate the oxidation activation energy and so on. But this method also has certain limitations. It is needed to combine with other analysis methods to better evaluate the performance of the lubricating oil, because of the difficulty to further analyze the trace oil sample being oxidated.

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