Thermal Oxidation Mechanism and Test Method of Lubricating Oil

Yuexing Wang¹,2, *, Yuanyuan Sun¹,2, * and Pujian Wang¹,2, b

¹State Key Laboratory of Intelligent Manufacturing of Advanced Construction Machinery, Xuzhou Construction Machinery Group, Xuzhou 221004.
²Jiangsu Xuzhou Construction Machinery Research Institute, Xuzhou Construction Machinery Group, Xuzhou 221004.

*Corresponding author email:sunyuanclcu.2009@163.com

Abstract. Thermal Oxidation Process Mechanism of lubricating oil is described, at the same time, the thermal oxidation test methods of lubricating oil-infrared spectrum, rotating oxygen bomb, Cyclic voltammetry and sludge content are introduced and compared. The correlation and difference between them were compared by experiments.

1. Introduction
The oxidation resistance of lubricating oil is an important index to reflect its quality, which determines the service life of lubricating oil and affects its service performance. Along with the mechanical equipment to the lubrication condition request rigor, also proposed the higher request to the lubricating oil thermal oxidation. During the oxidation of oil products, substances such as peroxide, alcohols, aldehydes, acids, esters and hydroxy acids are formed. These substances are further polymerized to form macromolecular compounds Adsorbed on the surface of the friction pair to form a paint film, further promoting the formation of carbon deposits or sludge [1]. Therefore, it is of great practical significance to increase the research on thermal oxidation performance and evaluation method of lubricating oil.

Modern Analytical and testing techniques must be used to determine the antioxidant properties of lubricating oils. According to the different antioxidant properties of lubricating oil, different methods can be used, such as: measuring the changes of antioxidant content in lubricating oil, such as Cyclic voltammetry, measuring the degradation of chemical properties, such as total acid value, total base value; Determination of changes in the chemical functional group content of lubricating oil, such as infrared spectroscopy; determination of oxidation time (temperature) of lubricating oil under high temperature and high pressure, such as rotating oxygen bomb; determination of sludge formation from oxidation of lubricating oil, such as weighing method of lubricating oil. These detection methods [2-3]focus on different, each has its advantages and disadvantages, there is a certain degree of correlation and consistency.

In this paper, the characteristics and correlation of infrared spectroscopy, rotating oxygen bomb method, residual antioxidant content (linear sweep voltammetry) and sludge test were discussed.
2. Experiment part

2.1. Detection method

2.1.1. Infrared spectroscopy. During the use of lubricating oil, due to oxidation, the formation of carbonyl oxides such as aldehydes, ketones, acids, esters, etc. The infrared spectra of used lubricating oil and new oil at 1850cm⁻¹~1550cm⁻¹ were measured and recorded by differential method [4]. The absorption value of used lubricating oil at 1720cm⁻¹ was calculated by the baseline method, which was the oxidation value of used lubricating oil.

2.1.2. Rotating oxygen bomb method. The method of rotating oxygen bomb is to put 50g oil sample, 5mL water and copper wire catalytic coil into a glass container with a cover and place it in the oxygen bomb with a pressure gauge. The oxygen bomb is oxygenated to (620±10) kPa, placed in a prescribed heater and rotated 30°-axis with the horizontal plane at a speed of 100r/min. The oxidation stability of the test is determined by the time (min) required for the test to reach the specified pressure drop (175 kPa).

2.1.3. Lubricating oils-determination of antioxidant content (ruler). Determination of antioxidant content in lubricating oil [5]. A linear sweep voltammetry was used to determine single or multiple antioxidants, and the qualitative analysis of antioxidants could be performed by Cyclic voltammetry. In neutral acetone-based Electrolyte, the characteristic peaks of aromatic amine type antioxidants are between 5s-12s and between 13s-16s, respectively. The oxidation life of lubricating oil was characterized by the determination of antioxidant content in lubricating oil.

2.1.4. Weighing method (sludge). Sludge content is to add 100g sample into the pumping filtration system after drying weighing to obtain the sludge content.

2.2. During the experiment

A lubricating oil sample was selected to oxidize oil and collect new and old oil before and after oxidation by a new type lubricating oil oxidation simulation test machine under the condition of air and high temperature.

The oxidation value of each oxidation stage was measured by using PE Company's Special Infrared Spectrometer. The oxidation stability was tested at 150 °C and 175 Kpa using Koller's rotating oxygen bomb tester, and the oxidation induction period was calculated. Use the Ruler Tester made by FLUETIC to test the consumption of antioxidants in lubricants at different times. The lubricating oil sludge is filtered and weighed by the self-made filter device in the laboratory.

3. Results and discussion

| Test Time | Oxidation value / A | Rotating oxygen bomb /min | Oxygen retention /% | Residual antioxidant /% | Oil sludge /mg.kg⁻¹ |
|-----------|---------------------|---------------------------|---------------------|-------------------------|---------------------|
| 0h        | 5.37                | 1030                      | 100                 | 100                     | 0                   |
| 100h      | 5.41                | 542                       | 52.6                | 98.6                    | 1.3                 |
| 200h      | 5.44                | 300                       | 29.1                | 64.2                    | 1.6                 |
| 300h      | 5.45                | 285                       | 27.7                | 84.4                    | 6.8                 |
| 400h      | 5.45                | 249                       | 24.2                | 74.2                    | 7.1                 |
| 600h      | 5.46                | 110                       | 10.7                | 47.5                    | 7.3                 |
| 800h      | 5.49                | 56                        | 5.4                 | 14.8                    | 7.8                 |
| 1200h     | 5.55                | 25                        | 2.4                 | 0                       | 11.6                |
3.1. Oxidation value measured by infrared spectroscopy

The oxidation mechanism of lubricating oil follows the oxidation mechanism of hydrocarbon. The modern oxidation mechanism of hydrocarbon is mainly based on Bach Adolf Engler's peroxide theory and Semionov's radical theory, which have been generally accepted. According to this mechanism, in the presence of molecular oxygen, the reaction follows the free radical chain reaction mechanism of

\[ RH \rightarrow R \cdot \]  
\[ R \cdot + O_2 \rightarrow RO_2 \cdot \]  
\[ RO_2 \cdot + RH \rightarrow ROOH + R \cdot \]  
\[ \Delta \text{ROOH} \rightarrow RO \cdot + \cdot OH \]  
\[ RO \cdot + RH \rightarrow ROH + R \cdot \]  
\[ \cdot OH + RH \rightarrow H_2O + R \cdot \]  

The oxidation of lubricating oil begins with equation (1). Lubricating oil is usually an alkyl (alkyl) substance containing hydrogen atoms written RH. Alkyl (alkyl) molecular groups R•, R• Form RO2•. With oxygen, peroxy molecular groups such as formula (2), R• Formed by the loss of hydrogen atoms due to various reasons such as heating, UV irradiation, shear stress or catalysis of metal ions. There is only a small change in the oil, and if a satisfactory antioxidant is present, the process can be delayed by a factor of 10, and the Peroxide Molecule reacts with the oil to Form Rooh hydroperoxide and R• Type (3). A key link in the self-accelerating oxidation process is equation (4). The high temperature decomposition of ROOH (about 150 °C above), and the decomposition products react with the lubricating oil again, such as the formation of alcohol-aldehyde-keto-acid in formula (5)(6).

![Fig. 1 Characteristic peak of infrared oxidation](image)

3.2. Sludge content

The oxidation of hydrocarbon molecules to various degrees produces a large number of oxygenated hydrocarbon compounds (7), such as alcohols, aldehydes, ketones, acids, etc. Causes the insoluble material to precipitate and the accumulation, the reaction mechanism is as follows.
3.3. Rotating oxygen rounds
In the presence of high temperature, air, iron, copper (Fe, Cu) and other catalysts, the decomposition of Rooh is easier, the reaction mechanism is as follows

\[
R \cdot + R \cdot \\
R \cdot + ROO \cdot \\
ROO \cdot + ROO \cdot \\
RO \cdot + R \cdot \\
\rightarrow \begin{cases} R - R \\
ROOR \\
ROOR \\
ROR \\
O_2 \end{cases}
\]  

(7)

3.4. Ruler-Antioxidant content
According to the formula for calculating the remaining service life of lubricating oil, the remaining service life of lubricating oil can be obtained at different test times:

\[
\%RUL = \frac{\text{Antioxidant dose of sample} - \text{amount of Blank Antioxidant}}{\text{amount of antioxidant in new oil} - \text{amount of blank antioxidant}} \times 100\%
\]

RUL = \%RUL \times \text{Usage time}

Fig. 2 shows the trend of residual antioxidants in the samples, 5s~8s being amine antioxidants and 13 s~16 s being phenolic antioxidants. It can be seen from the graph that the consumption of type antioxidants begins after the consumption of type antioxidants. The service life of phenol Amine Antioxidant synergism is longer than when used alone. The results showed that when the content of antioxidant remained about 15 %, the sludge increased suddenly.

![Fig. 2 Ruler antioxidant content](image-url)
Fig. 3 Synergistic mechanism of phenolic amine antioxidants

Antioxidants are added to oils to capture the free radicals \( R\cdot \) and \( R\text{OO}\cdot \) formed during the chain reaction phase so that they do not cause destructive chain reactions. According to the mechanism of action, antioxidants are generally divided into main antioxidants and auxiliary antioxidants. The main antioxidant can react with radical \( R\cdot \) and \( R\text{OO}\cdot \) and interrupt the growth of the active chain. The assistant antioxidant can inhibit and delay the generation of free radicals in the initiation process. Fig. 3 shows the typical synergistic mechanism of phenolic amine antioxidants.

Fig. 4 Variation trend of oxygen bomb number-antioxidant-sludge in sample A

3.5. Summary
By analyzing the relationship among the change value of rotating oxygen bomb, the change value of antioxidant content and the increase of oil sludge, it is found that the decrease trend of rotating oxygen bomb and the decrease trend of antioxidant basically have a good correlation, as shown in Fig. 4. The trend chart shows that the content of oxygen bomb and antioxidant decreased sharply in the first 200 h, the phenolic antioxidant degraded and the amine antioxidant remained. The 200 h sudden increase of the sludge showed that the oxidant was partly changed. When the oxygen bomb of oil is kept at about 25 %, the antioxidant remains 74.2 %, and the sludge has not changed significantly, so the oxidation experiment can continue. At 600 h, the oxygen bomb decline rate is only 10.7 %, the antioxidant is 47.5 %, the change of sludge is not obvious, which shows that the oil still has good oxidation performance. The content of antioxidant remained 14.8 % at 800 h, and the sludge increased sharply from 800 h, which could be used as a turning point of oil. When the oil sludge exceeded the requirement of the index at 1200 h, the content of antioxidant was 0 %, which indicated that the oil had no anti-oxidation property.

To sum up, the oil still has good oxidation stability with the decreasing value of rotating oxygen bomb kept at 25 %. Combined with the test of the remaining content of antioxidant, the oxidation property of the oil can be maintained. Increase the safe use limit by 10 %, can choose to antioxidant residual content of 25 % for oil life warning line.
4. Conclusion
As a common index to measure the oxidation degree of oil, the oxidation stability of oil determined by rotating oxygen bomb method is related to the content of antioxidant in lubricating oil, which can be used as an assistant means to detect the oxidation of lubricating oil. However, with the requirement of anti-oxidation of lubricating oil for construction machinery, the oxidation stability of lubricating oil after adding anti-oxidation agent is generally higher, and the monitoring standard of residual oxidation capacity greater than 25 % [9] of new oil is no longer applicable.

Infrared analysis is a very effective means to monitor the status of oil. It can not only analyze the consumption of antioxidants, especially phenolic antioxidants, but also observe the oxidation of oil. It has some interference to the determination of amine antioxidant.

The Ruler analysis, as a specialized method for measuring changes in antioxidant content, is useful for monitoring the consumption of phenolic and amine antioxidants commonly used in lubricating oils during operation. There is a correlation between the decrease of oxygen bomb and the decrease of oxygen bomb.

Different antioxidant assay methods have their own characteristics and should be considered comprehensively according to specific research problems. The oxidation resistance of the whole oil antioxidant system was investigated by rotating bomb, but the real induced termination point could not be identified by software. Infrared and Ruler are fast and convenient, which can reflect the consumption of antioxidants. Therefore, in order to comprehensively investigate the antioxidation performance of lubricating oil, it is necessary to evaluate the antioxidation performance of lubricating oil by various testing methods.

References
[1] Xue Weiguo, Li Jianming, Zhou Xuguang. Research progress of lubricant antioxidant. Dalian Lubricant Technology and Economy Forum 2011,220-228.
[2] Yimeirong. Study on test method of oxidation stability of turbine oil. Lubricants, 2012,27 (3): 28-37.
[3] Fei Yiwei, Kwok Fung, et Al. Comparison and analysis of standard test methods for thermal oxidation stability of lubricating oils. Journal of Chemical Engineering, 2015,29 (2):37-42.
[4] Long Fen. Application of infrared spectrum in determination of multi-type antioxidant content in lubricating oil. Chemical Engineering, 2010,8:190-196.
[5] Shi Yonggang, Wang Deyan, Ma Yan. Lubricating oils-determination of Antioxidant content-Cyclic voltammetry. Lubrication and sealing, 2004,3:33-37.
[6] Jezl J L, Stuart A P, Schneider Abraham. Interrelated Effects of Oil Component ion Oxidation Stability. IndEnChem.1958,50 (6):947-950.
[7] Wang Lijuan, Liu Weimin. Mechanism of action of lubricant antioxidant. Lubricants, 1998, 13 (2): 55-58.
[8] Vincent J Gatto, William E Moehle. Oxidation Fundamentals and Its Application to Turbine Oil Test [C]/Journal of ASTM International.
[9] Qian Yihua, Meng Weixin, Wang Hongmei. Experimental study on the relationship between oxidation of turbine oil and film formation. Thermal power generation, 2017,46 (5): 122-126.