Study on the Influence of Antioxidants on Transformer Oil Related Indicators

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Abstract. 2,6-di-tert-butyl-p-cresol (T501) is the most commonly used antioxidant for insulating oils. It has been found that the amount of T501 added to the insulating oil affects the physical and electrical properties of the insulating oil. In this paper, the effects of antioxidants on insulating oils at different concentrations were studied. The research focused on acid value, water-soluble acid or alkali, flash point, kinematic viscosity, volume resistivity and interfacial tension. An aging test was conducted at 115°C to test changes in acid value, sludge, and volume resistivity. Add the same quality insulating paper to the oil sample with the blank oil and T501 added in the amount of 1% (mass fraction), and isolate the oxygen to the effect of furfural before and after the addition of the antioxidant after aging at 130 °C. The results show that with the increase of the amount of antioxidant T501, the interfacial tension, acid value and electrical resistivity will decrease its performance index, but the effect on flash point, viscosity and pour point is not obvious. The aging test by heating the open cup shows that the antioxidant has an obstructive effect on the acid value and the sludge, delays the aging of the insulating oil, but accelerates the aging hydrolysis of the insulating paper. Therefore, it is recommended that the antioxidant content in the insulating oil should not be excessively added. In the insulating oil, the proportion of the antioxidant in the insulating oil should be reduced on the premise that the oxidation resistance can be achieved, and the T501 part consumes the logistics.

1. Introduction
At present, the oil-immersed transformer is the core equipment in the power transmission and transformation system, and the reliability of the insulation system plays a vital role in the stable operation of the equipment. The oil-immersed transformer insulation system is mainly composed of insulating paper and insulating oil. During the long-term operation of the transformer, due to the synergistic influence of temperature, moisture and other factors, the oil-paper insulation system is gradually aging, which may lead to insulation failure [1-4]. The failure of electrical equipment is often caused by the deterioration of the insulation effect of insulating oil and insulating paper. The aging failure of insulating paper is a key indicator to determine the service life of the transformer. Although transformer oil-paper insulation aging is the result of a combination of factors, the life of transformer main insulation, that is, the life of oil-paper insulation is actually determined mainly by its thermal aging, which is the most important factor in many aging factors [5]. The heat generated during the operation of high-voltage electrical equipment causes the insulation temperature to rise, causing physical and chemical changes that deteriorate and age the insulation material. Therefore, it is necessary to add a certain amount of antioxidant to the insulating oil. There are many types of
antioxidants, including amine antioxidants, phenolic antioxidants, phosphorus-containing antioxidants, and thioester antioxidants. However, the most widely used and most effective antioxidant for minerals is T501. At present, an antioxidant widely used in China’s transformer oil is also T501. T501 has good anti-oxidation effect, low price, stability and safety. It is widely used in food, plastics and synthetic rubber. It is the most demanding type of phenolic antioxidant. It accounts for 30%, 40%, and 50% of phenolic antioxidants in Japan, the United States, and Europe, respectively. However, T501 mainly plays a role in the oxidation induction period of oil, and the content in the aging process will continue to decrease, and it is difficult to play a good anti-aging effect in the middle and late stages of oil aging. At present, the content of antioxidants in insulating oil at the time of domestic new oil acceptance is 0.08% ~ 0.4%. For transformers that have been in operation for some years, if the content of the insulating oil is less than 60% of the original value of the new oil, the antioxidant should be added. Many researchers have done a lot of research on the optimal addition amount of antioxidants in transformer oil, and it is determined that in actual engineering, when the antioxidant content in the transformer oil drops to 0.15%, the antioxidant is added to increase the content to 0.3% ~ 0.4% to achieve the best antioxidant effect [6, 7].

T501, also known as 2,6-di-tert-butyl-p-cresol, has the following structural formula:

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T501 is a colorless to white crystalline or crystalline powder. It is basically tasteless and easily soluble in petroleum ether, ethanol, mineral oil, and the like. It does not color when reacted with metal ions, and has a sublimation property of a monophenol type, and volatilizes together with water vapor upon heating. T501 is synthesized from cresol and isobutylene as a raw material. It belongs to the third type of antioxidant, which is added in the initial stage of oxidation or oxidation of oil, and has the effect of inhibiting oxidation. The molecule contains an active hydroxyl group, which can inhibit the oxidation of oil and provide a hydrogen atom to combine with peroxy radicals. The mechanism of inhibiting oxidation of oil is as follows:

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Due to its superior performance, it still dominates the hindered phenolic antioxidants and can be added to food oils and lubricants [8].

At present, the research on antioxidants in transformer oil mainly focuses on the measurement of antioxidant content [9-10], and the determination of the optimal addition amount, but the research on the physical and electrical indexes of transformer oil for the amount of antioxidant added is relatively less. In this paper, the effects of different mass fractions of antioxidants on the physical and electrical properties of insulating oil were analyzed. Then, the change of acid value and sludge in insulating oil with different concentrations of T501 after aging at 115°C was studied by open cup aging test. The blank insulating oil and the insulating oil with a T501 concentration of 1% were set to accelerate aging at 130°C. The effect of the antioxidant on the aging of the insulating paper was investigated by measuring the content of furfural in the oil.

2. Experiment

2.1. Experimental materials
In the course of this experiment, the materials used were #25 insulating oil (without added antioxidant) produced by Sinopec Great Wall Lubricating Oil Company; analytical pure methanol; analytical pure 2,6-di-tert-butyl-p-cresol; Insulating paper tape of 0.1 mm thickness; 500mL high temperature aging tank (with pressure reducing valve).

2.2. Experimental plan
At present, in China’s standard “Transformer Oil (General) Technical Requirements and Test Methods”, the antioxidant content in the new oil is divided into anti-oxidation additive oil (not detected) and micro-antioxidant additive oil (not more than 0.08%). And oils containing antioxidant additives (0.08% to 0.4%). In practice, some of the transformers have an antioxidant content of more than 0.4%. Considering the experimental concentration gradient, the ratios of 0.1%, 0.3%, 0.5%, and 1% (mass fraction) are selected, and a set of antioxidant-free blanks is added. The experimental group served as a control.

This paper designs three sets of experiments:
(1) The oil samples of the five antioxidant concentrations that have been configured are tested for moisture, interfacial tension, pour point, flash point(closed), volume resistivity, acid value and viscosity. Study the effects of antioxidants on the physical and electrical properties of transformer oil.
(2) Perform an open cup aging test on transformer oils with five antioxidant contents. Five clean beakers were added, and 400g of oil samples of different antioxidant contents were added to each beaker, and 66cm of spiral copper wire (which had been polished) was placed, and placed in a 115° C blast oven for 72 hours. After taking out and cooling, the acid value in the oil was measured, and the sludge deposition test was performed.
(3) The test was carried out by taking a blank oil sample and a transformer oil with a concentration of 1% antioxidant to study the effect of antioxidant on the aging of the insulation paper. Cut the insulating paper strip into 2cm equal length segments, 8g of each weighing is placed in 4 high-temperature aging tanks with a volume of 500mL, numbered A, B, C, D. Add 200g of blank insulating oil to A and C, add B and D 200g of insulating oil with an antioxidant concentration of 1%. Nitrogen is introduced into A and B, the air in the aging tank is completely exhausted, and the lid is quickly tightened under a nitrogen atmosphere. It was placed in a blast drying oven at 130°C and taken out after 72 hours. After the oil sample is cooled, 10 mL of insulating oil is added to 2.5 mL of methanol. After shaking and centrifuging, the high-performance liquid chromatograph was used to detect the insulating oil in the A, B, C, D tanks and the non-aged blank insulating oil and the concentration of the antioxidant in the 1% insulating oil.

3. Test results and analysis
3.1. Physical and electrical indicators of insulating oil
In the transformer new oil acceptance and transformer troubleshooting, the physical and chemical indicators and electrical indicators of the insulating oil are tested, including moisture, interfacial tension, flash point (closed), kinematic viscosity, pour point, volume resistivity, acid value, Water soluble acid is tested. Moisture in insulating oil is a very important indicator, and moisture control is very strict before it is put into operation. The presence of moisture not only reduces the insulation properties of the insulating oil but also accelerates the aging of the insulating oil and the insulating paper, reducing the service life of the transformer. The interfacial tension is mainly to detect the bonding ability of insulating oil and water, and also to reflect the cleanliness of insulating oil. The good separation of water can prevent the rapid deterioration of insulating oil. The closed flash point is from the perspective of fire prevention, because when the transformer fails, it is often accompanied by arc or high temperature. As the temperature rises, the oil and gas evaporated on the surface of the fuel increases. When the mixture of oil and gas reaches a certain concentration, A short flash of light will occur when exposed to an open flame. Flash point is an important indicator to prevent fires in insulating oil. Insulating oil not only has the function of insulation, but also has the ability to dissipate
heat, so the insulating oil must have a certain kinematic viscosity. The pour point is also referred to as the lowest cold operating temperature. When the temperature is too low, the insulating oil will solidify, so the pour point of the insulating oil is determined according to the historical minimum temperature of the location of the transformer. Volume resistivity mainly reflects the insulation performance of insulating oil is an important electrical indicator. The acid value is often controlled in the insulating oil, because the acid value will greatly affect the service life of the insulating oil and the insulating paper. The large acid value will accelerate the deterioration of the insulating oil to produce sludge, accelerate the hydrolysis of cellulose in the insulating paper, and reduce the transformer. Service life. The water-soluble acid is a low molecular organic acid and an inorganic acid which are soluble in water in the oil. When the water-soluble acid and alkali are unqualified, not only the equipment is corroded, but also the withstand voltage of the transformer is lowered.

By adding different quality T501 antioxidants to the insulating oil, five different concentrations of insulating oil samples with antioxidant contents of 0%, 0.1%, 0.3%, 0.5%, and 1% were prepared, and the acid value, moisture, interfacial tension, and the flash point (closed mouth), volume resistivity, kinematic viscosity, water-soluble acid or alkali and pour point are tested. The following trend chart shows the effect of antioxidants on the physical and electrical properties of insulating oil.
Figure 1. Trend diagram of physical and electrical indicators of insulating oil

From figure 1, it can be found that the addition of a certain amount of antioxidant T501 has no significant effect on the water content of the insulating oil, the flash point (closed), the water-soluble acid or alkali, and the physical index of the pour point; The tension and resistivity showed a linear decline trend; for the insulating oil, the kinematic viscosity showed a trend of increasing first and then stabilizing. The acid value of the insulating oil shows a linear upward trend. The antioxidant di-tert-butyl-p-cresol (T501) is a phenolic substance in the insulating oil. Since the hydroxyl group and the benzene ring interact with each other, the phenolic hydroxyl group can have a certain degree of ionization. It is weakly acidic, so as the content of T501 increases, the acid value in the insulating oil will also become larger.

3.2. Open cup aging test

After the material beaker was taken out from the blast drying oven, the acid value and sludge deposition test were carried out respectively. The test data are shown in the table 1:

| T501 content | 0%  | 0.10% | 0.30% | 0.50% | 1.00% |
|--------------|-----|-------|-------|-------|-------|
| Acid value   | 0.055 | 0.011 | 0.008 | 0.010 | 0.015 |
| Sludge precipitation | Sludge | Sludge | Sludge | Sludge | Sludge |
| colour       | light yellow | Transparent | Transparent | Transparent | Transparent |

It can be seen from the table 1 that after the aging of the open cup at 115 °C for 72 h, the insulating oil without adding antioxidant is seriously aged, the acid value is increased a lot, and sludge is produced. In the insulating oil to which an antioxidant is added, the acid value is also high when the content is too large. Since di-tert-butyl-p-cresol makes the insulating oil weakly acidic, the aging rate of the oil is accelerated at an elevated temperature to cause an increase in the acid value. Therefore, the amount of antioxidant added must be appropriate, and the excess will have the opposite effect on the oil.

3.3. The effect of antioxidants on oil-paper insulation system

In order to study the effect of antioxidants on insulating paper, two sets of tests were set up, which are the changes of furfural under aerobic conditions and anaerobic conditions. As shown in the following table 2:

| No.       | A           | B           | C           | D           |
|-----------|-------------|-------------|-------------|-------------|
| Furfural content before aging | 0           | 0           | 0           | 0           |
| Furfural content after aging  | 1.0821      | 0.8823      | 0.0467      | 0.1013      |
It can be seen from the table 2 that when the oil-paper insulation system is not isolated from the air, the insulation paper without the antioxidant T501 is more deteriorated; and when isolated from the air, the insulation of the insulation paper can be greatly reduced, but the insulation is added. The content of furfural in oil is higher than that in insulating oil without antioxidant. It is considered that the weakly acidic antioxidant at normal temperature is similar to the acceleration of aging of insulating paper by other organic acids, which will ionize hydrogen ions. The ionization process is as shown in equation (3), and an increase in temperature causes an increase in the degree of ionization. The higher the content of T501 added to the oil, the greater the amount of ionized hydrogen ions, and the stronger the ability to promote the hydrolysis and degradation of cellulose. This is because the aging rate of the insulating paper in the experimental group is much larger than that of the control group. the reason.

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R \cdot \text{OH} \leftrightarrow R \cdot O^- + H^+ \quad (3)
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4. Conclusion
In this paper, for the addition of different T501 concentration of insulating oil, the insulating oil was first tested for moisture, interfacial tension, flash point (closed), kinematic viscosity, pour point, volume resistivity, acid value, and water-soluble acid. The influence of physical and chemical indicators and electrical indexes of insulating oil; then the open cup aging test of insulating oil, the change of acid value in insulating oil and the production of sludge, the influence of antioxidant on the aging of insulating oil; the final application of insulating oil and the insulation system consisting of insulating paper is the same as the air contact and air-insulated accelerated aging test. After 72 hours, the furfural in the insulating oil is tested to analyze the effect of the antioxidant on the aging of the insulating oil and the insulating paper:

1. The antioxidant T501 has no obvious influence on the water content, flash point (closed), water-soluble acid or alkali, and physical index of the pour point of the insulating oil; the interfacial tension and electrical resistivity of the insulating oil show a linear decline trend; The kinematic viscosity of the insulating oil shows a trend of increasing first and then stabilizing. It can be instructive for the addition of antioxidants in insulating oils.

2. The insulating oil without adding an antioxidant is severely aged, the acid value is increased a lot, and sludge is generated. In the insulating oil to which an antioxidant is added, the acid value is also high when the content is too large. Therefore, the amount of antioxidant added to the insulating oil should be appropriate and take the form of “diligent addition and less addition”.

3. It is found that the addition of antioxidant T501 makes the insulating oil weakly acidic. Under the heated condition, the phenolic hydroxyl group will ionize more hydrogen ions, which will accelerate the hydrolysis of the insulating paper and reduce the service life of the transformer.

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