

Overview of Oxidation Stability Test of Vegetable Based Insulating Oil

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Abstract

Vegetable based insulating oil is a green substitute for mineral insulating oil, which has poor oxidation stability. Thus, oxidation stability is a key index for its popularization and application, while there is no corresponding test method. This work summarized the oxidation mechanism, process of vegetable based insulating oil, and current test methods of oxidation stability used in vegetable oil or traditional mineral oil. By comparing those methods, an improved method based on Rancimat method was proposed, which was more suitable for vegetable based insulating oil. This work has made a certain contribution to the promotion of green and sustainable materials.

Keywords

Vegetable based insulating oil; Green material; Oxidation stability; Rancimat method; Catalysis of copper.

1. Introduction

Insulating oil (or transformer oil) is a liquid dielectric that is widely used for electrical equipments, such as transformers, due to its insulation, cooling, and arc suppression effects [1, 2]. For a century, mineral oil has firmly dominated the insulating oil market given its good insulation, heat dissipation properties, and inexpensive cost [3]. However, as a petroleum product, mineral oil is toxic, poorly biodegradable, and non-renewable. In the event of any leakage, mineral oil is prone to pollute the environment or leave hidden fire safety problems [4]. With the improvement of people's environmental awareness, the defects of mineral oil have been increasingly criticized [5]. Then, vegetable oil, a non-toxic, degradable, and renewable resource, was taken as a green substitute for mineral oil by researchers all over the world [6-9].

Until now, vegetable oil based dielectrics (natural esters) have been used in transformers for about twenty years [10]. There are mainly three products: Envirotemp FR3® fluid, BIOTEMP® fluid and Midel® eN fluid, replacing mineral oil based products in the marketplace increasingly [11-13]. All the natural ester products have shown excellent electrical properties as liquid dielectrics. Moreover, their flash point is about 300 °C, which is much higher than that of traditional mineral oil (about 150 °C). Thus, vegetable oil dielectrics are less flammable and much safer in term of fire hazard. However, compared with mineral insulating oils, natural ester dielectrics are significantly weak in oxidative stability, even if antioxidants have been added in the products. Therefore, the oxidation stability of vegetable based insulating oil need to be paid more attention. However, there is no suitable test method for oxidation stability of vegetable based insulating oil.

This work summarizes the oxidation stability of vegetable based insulating oil and current determination methods used in vegetable oil or traditional mineral oil. The limitations of various test methods are compared to select the most suitable method. Accurate evaluation of

oxidation stability is helpful for the wider application of vegetable based insulating oil as a green material.

2. Oxidation Process and Oxidation Stability of Insulating Oil

For a long-term use, insulating oil will decompose under the action of oxygen to produce free radicals. Then some oxidation products with small molecular are generated through a series of free radical reactions. These oxidation products will be enriched continuous in the oil, and eventually change the properties of the oil. This process is called oil oxidation (or aging and deterioration) [1].

During the oxidation process, insulating oil will produce acidic substances, which will corrode metal parts, shorten the service life of equipment and affect the safe operation of equipment; Some precipitates such as oil sludge will also be generated to increase the viscosity of insulating oil and reduce its cooling, heat dissipation and lubrication effects; Some polar substances will also be generated, which will seriously reduce the dielectric loss, breakdown voltage and other electrical properties of insulating oil, resulting in serious heating, dielectric breakdown and other faults. Sometimes, it may cause major equipment and personal accidents. Therefore, in a long-term use of electrical equipment, the stability of properties of insulating oil is very important.

Oxidation stability is used to characterize the stability of insulating oil in a oxidation process. The better oxidation stability means that the slower the oxidation process of oil under the same environment, the longer the service life.

2.1. Mechanism of Oxidation Process of Vegetable Based Insulating Oil

The oxidation mechanisms of mineral oil and vegetable oil are both chain free radical reaction, including three stages: chain initiation (generation of free radical), chain transfer (transfer of free radical) and chain termination (recombination of free radical) [14]. According to the classical free radical reaction theory, chain initiation is the most difficult step, which controls the rate of the whole free radical reaction. Because of a large number of unsaturated fatty acid chains in vegetable oil. The hydrogen atom at α -position of carbon carbon double bond is easy to be attacked by oxygen to form a stable conjugated structure with three electrons and three centers similar to propylene radical [15]. Due to the conjugated structure formed by free radical electrons and double bonds reduces the activation energy of chain initiation reaction, oxidation process of vegetable oil is easy to occur. Therefore, the oxidation stability of vegetable based insulating oil is significantly weaker than that of mineral insulating oil composed of saturated hydrocarbon and aromatic hydrocarbon.



Figure 1. Chain initiation reaction of oxidation of vegetable based insulating oil.

2.2. Changes of Vegetable Based Insulating Oil During Oxidation

The oxidation process of insulating oil can generally be divided into induction period, development period and hysteresis period [16]. In the initial stage of oxidation, the free radicals generated by chain initiation did not directly guide the chain transfer reaction, but generated secondary peroxides (ROOR or ROOH). The radical generated by the decomposition of these peroxides is the initiation center of the new chain. However, peroxide decomposition requires a period of time, which is called induction period. During the induction period, the oxidation process of insulating oil is very slow, and the oil slowly absorbs oxygen and forms various peroxides. In this stage, the peroxide value increases significantly, but the oxidation products are rarely produced, and the appearance and smell of the oil will not change significantly.

Generally, the longer the induction period of vegetable insulating oil, the better its oxidation stability.

After the induction period, it is the development period. In this stage, the chain transfer process begins, and the insulating oil absorbs oxygen rapidly, which intensifies the oxidation. These free radicals decompose rapidly while forming peroxides to produce stable oxidation products, such as small molecular aldehydes, ketones, short chain fatty acids and so on. The oxidation products at this stage are soluble in oil and water, with strong corrosion and obvious smell. The acid value and conductivity of the oil will increase significantly, but the peroxide value will decrease. While the oxidation continues, it will enter the hysteresis period. During this period, the oxidation rate gradually slows down and the oxidation products also slowly decrease. The low molecular oxidation products will undergo polymerization and polycondensation reactions to form solid polymers and condensates. When they reach the saturation state in the oil, they will precipitate from the oil, which is usually called oil sludge. During the hysteresis period, the viscosity of vegetable based insulating oil will obviously increase and the color will become darker. When the polymerization reaction is serious, the natural ester even lose its fluidity and form colloidal solid.

3. Factors Affecting Oxidation Rate of Vegetable Based Insulating Oil

3.1. Fatty Acid Composition of Vegetable Oil

It was been reported that in vegetable oil, the higher the degree of unsaturated fatty acids, the worse the oxidation stability. The relative oxidation rate of linolenic acid, linoleic acid and oleic acid is about 25:12:1 [17].

3.2. Oxygen

The oxygen partial pressure in transformer and the contact mode with insulating oil are important factors affecting the oxidation of insulating oil. According to the poor oxidation stability of vegetable based insulating oil, some researchers designed closed transformer filled with nitrogen to slow down the oxidation process.

3.3. Temperature

According to the principle of chemical kinetics, the higher the temperature, the faster the rate of chemical reaction. The oxidation reaction of vegetable based insulating oil is no exception. When the temperature increases by 10 °C, the oxidation rate of insulating oil will be doubled.

3.4. Catalyst

Some studies have shown that copper ion will accelerate the oxidation process of vegetable oil as catalyst, while iron ion has no obvious catalytic effect [18]. Copper core is an indispensable component in transformer. Therefore, the catalytic effect of copper ion on plant-based insulating oil can not be ignored.

3.5. Antioxidants

Antioxidants can inhibit the oxidation reaction to a certain extent. In fact, both traditional mineral insulating oil and vegetable based insulating oil are added with antioxidants to prolong the service life of the product.

4. Test Method for Oxidation Stability

As a new material, vegetable based insulating oil has no special oxidation stability test standard in power industry. With reference to the common test methods of mineral oil, vegetable oil and

vegetable oil fatty acid ester, they can be divided into the following four types according to the test objects or indicators.

4.1. Substrate Test Method

This method detects the changes of substrate properties in oil oxidation. The oxidation stability of oxidized oil can be judged by the changes of acid value, sludge precipitation or oxygen absorption of oxidized oil. SH/T 0206 (a petrochemical industry standard of China), is one of the substrate test methods. The method is to add copper wire catalysis under the environment of heating and continuous oxygen-containing atmosphere to make the oil sample oxidize rapidly, and evaluate the oxidation stability of the oil sample through the changes of insoluble matter (oil sludge) produced and the acid value of the oil.

4.2. Peroxide Test Method

This method detects the intermediate product - peroxide, in the process of oil oxidation. The oxidation stability of oil can be judged by measuring the change of peroxide content through reduction reaction. Among these methods, the most classic active oxidation method (AOM) has been designated as the official detection method by many organizations, but it has been rarely used in recent years due to the disadvantages of complex operation, long test cycle and unstable peroxide content [19].

4.3. Volatile Matter Test Method

Those methods detect small molecule volatile products produced by oil oxidation. The content of these volatile substances can be detected, and the induction period of oil oxidation can be judged by their content change. Rancimat method is the most classic one among these methods, which is also called conductivity method. In Rancimat method, oils were oxidized to produce the final products of small molecule volatile products in a strong oxidation condition. Those volatile products were absorbed into deionized water through a absorption tank, and the oxidation induction period could be calculated by the conductivity change of water in the tank. For instance, GB/T 21121 (a national standard of China) is a typical Rancimat method used in the determination of oxidative stability of animal and vegetable oils and fats.

4.4. Thermal Analysis Method

Those methods judge the reaction process through the change trend of thermal effect in oxidation process. The induction period or initial oxidation temperature could be obtained as the index to evaluate oxidation stability. However, oxidation in normal environment is a very slow process, and its thermal effect is not obvious. Using conventional thermal analysis methods, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), the thermal effect in the oxidation process can not be accurately detected. At present, high pressure differential scanning calorimetry (PDSC) was used to estimate the oxidation stability of oil products in some standards, such as ASTM d 6186, ASTM d 5483, etc.

4.5. Discussion

Substrate test method was often used to test the oxidation stability of traditional mineral oil. However, due to the weak oxidation stability of vegetable insulating oil, the substrate change in vegetable oils is too sharply to distinguish. Peroxide test method is not a good choice because of its complex operation, long test cycle and unstable peroxide content. Volatile matter test method, especially Rancimat method, provides a mild oxidizing environment which is suitable for vegetable oils. However, the existing standards of Rancimat method cannot simulate the working environment of insulating oil. Specially, the catalytic effect of copper has not been considered in those methods. Thermal analysis method, mainly PDSC method, requires special instruments which could only provide a closed oxidation environment with high oxygen pressure. And the thermal effect of oxidation process will be disturbed by other chemical

reactions, such as thermal decomposition and volatilization. The results of PDSC test were often taken only as reference.

Therefore, volatile matter test method (Rancimat method) is the most suitable method for vegetable oil. But for vegetable based insulating oil, test process needs to be improved. Copper coil should be soaked in vegetable oil when the test was carried out.

5. Conclusion

Due to the presence of unsaturated fatty acids, the oxidation stability of vegetable based insulating oil is weaker than that of traditional mineral oil. Thus, the oxidation stability of vegetable based insulating oil is an important performance which needs to be accurately evaluated, while there is no suitable test method. By comparing the existing oxidation stability test methods, traditional test methods for mineral insulating oil were not fit for their strong oxidation conditions or inappropriate targets. While the methods for edible oil ignored the work environment of insulating oil. Comprehensive consideration, a method based on the Rancimat method, which add copper wire to the oxidation process, is a more appropriate choice, compared with the existing methods. A suitable test method for oxidation stability of vegetable insulating oil is more conducive to its popularization and application as a green and sustainable material.

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