

Review of Research Progress on the Electrical Properties and Modification of Mineral Insulating Oils Used in Power Transformers

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Date Submitted: 2020-02-24

Keywords: power transformer, molecular dynamics simulation, electrical properties, mineral insulating oil

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Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version):

LAPSE:2020.0261

Citation (this specific file, latest version):

LAPSE:2020.0261-1

Citation (this specific file, this version):


LAPSE:2020.0261-1v1

DOI of Published Version: <https://doi.org/10.3390/en11030487>

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Review

Review of Research Progress on the Electrical Properties and Modification of Mineral Insulating Oils Used in Power Transformers

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Received: 29 January 2018; Accepted: 19 February 2018; Published: 26 February 2018

Abstract: In November 2017, the first ± 1100 kV high-voltage direct-current power transformer in the world, which was made by Siemens in Nurnberg, passed its type test. Meanwhile, in early 2017, a ± 1000 kV ultra-high voltage (UHV) substation was officially put into operation in Tianjin, China. These examples illustrate that the era of UHV power transmission is coming. With the rapid increase in power transmission voltage, the performance requirements for the insulation of power transformers are getting higher and higher. The traditional mineral oils used inside power transformers as insulating and cooling agents are thus facing a serious challenge to meet these requirements. In this review, the basic properties of traditional mineral insulating oil are first introduced. Then, the variation of electrical properties such as breakdown strength, permittivity, and conductivity during transformer operation and aging is summarized. Next, the modification of mineral insulating oil is investigated with a focus on the influence of nanoparticles on the electrical properties of nano-modified insulating oil. Recent studies on the performance of mineral oil at molecular and atomic levels by molecular dynamics simulations are then described. Finally, future research hotspots and notable research topics are discussed.

Keywords: mineral insulating oil; electrical properties; power transformer; molecular dynamics simulation

1. Introduction

Insulating oil is widely used as an insulating medium in oil-immersed transformers, allowing the safe and reliable transmission of electrical energy. The first insulating oil applied to transformers was mineral oil extracted from petroleum [1]. Since the 1940s, mineral insulating oil has been widely used in power equipment like transformers, capacitors, cables, and bushings [2].

With the development of science and technology, more and more types of transformer oil have been developed, but mineral insulating oil is still used widely because of its low cost, good insulating properties, low condensation point, and low viscosity. At present, the main raw materials of mineral insulating oil are paraffin-based and naphthenic-based crude oils [3], which are composed of hydrocarbons. The hydrocarbon components include alkanes, cycloalkanes (one-, two-, three-, and four-membered rings), and aromatic hydrocarbons. The two main components are alkanes and cycloalkanes [4], and the only difference between crude oils is the proportion of each component. The specific charts showing the classification and an introduction about different types of insulating oils can be found in reference [2].

1.1. Characteristics of Naphthenic-Based Mineral Insulating Oil

The molecular structures of the main components of the naphthenic-based oils are shown in Figure 1. Important features of naphthenic-based mineral insulating oil are summarized as follows.

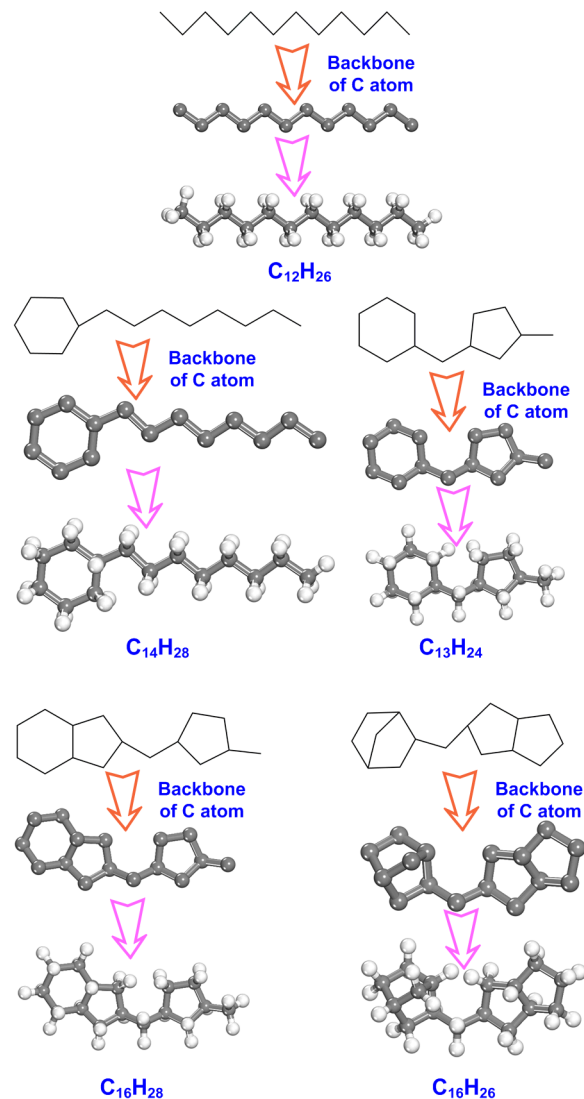


Figure 1. Main components of naphthenic mineral insulating oil.

1.1.1. Suitable Solubility

Naphthenic-based insulating oil has moderate solubility, and can not only dissolve the oil sludge generated from the compound actions of high temperature, electric field, moisture, and metal catalysts, but also prevent the insulating varnish of the transformer from dissolving [5]. Because the naphthenic-base oil can dissolve the oil sludge, it prevents the oil sludge from sticking onto the insulating material and depositing on the circulating oil ducts and cooling fins, helping to avoid the local overheating of the transformer winding and the rise of the transformer operation temperature, prolonging the service life of the transformer.

1.1.2. Good Low-Temperature Properties

The low-temperature environment suitable for the use of transformer oil can be estimated from its pour point. Because paraffinic-based oil contains more paraffin hydrocarbons, which readily crystallize

at low temperature, than naphthenic mineral insulating oil, the fluidity of the oil decreases. If the pour point of paraffinic-based oil is lowered through dewaxing, its cost is comparatively high, and the pour point cannot be very low because of the restriction of degree of dewaxing. Compared with that of paraffinic-based oil, the content of paraffin hydrocarbons in naphthenic-based transformer oil is low, and its pour point is low without dewaxing [3]. Therefore, naphthenic-based transformer oil is endowed with good low-temperature properties. In the case of an extreme climate with temperatures as low as $-40\text{ }^{\circ}\text{C}$, naphthenic-based transformer oil still works normally without affecting the insulation properties of the equipment.

1.1.3. Favorable Heat Dissipation

Generally, the high-temperature viscosity of transformer oil needs to be as low as possible to maximize the fluidity and aid heat emission. Some research data show that the kinematic viscosities of naphthenic-based and paraffin-based transformer oils at $40\text{ }^{\circ}\text{C}$ are similar. However, when the temperature reaches $100\text{ }^{\circ}\text{C}$, the kinematic viscosity of naphthenic-based transformer oil is obviously lower than that of the paraffin-based transformer oil. Therefore, when naphthenic-based oil is used, the heat dissipation and cooling properties of the transformer will be better. QS2598A paraffinic-based oil and V-35 standard naphthenic-based oil have been researched [6]. It was found that the viscosity of naphthenic oil is much lower than that of paraffin-based crude oil when the temperature is $-20\text{--}50\text{ }^{\circ}\text{C}$. This shows that normal starting with naphthenic transformer oil is easier than that with paraffinic transformer oil in winter after stopping [3]. Although naphthenic crude oil possesses a variety of good performance parameters, naphthenic-based crude oil is a rare resource and only accounts for 2–3% of the total amount of crude oil [7]. Since the petroleum crisis in the 1970s, the naphthenic-based crude oil resource has gradually decreased [8]. In the 1980s, production of naphthenic-based crude oil rapidly lowered to only 20% of that in 1970s [9].

1.2. Characteristics of Paraffinic-Based Transformer Oil

The molecular structures of the main components of paraffinic-based oil are shown in Figure 2. Important features of paraffinic-based transformer oils are summarized as follows.

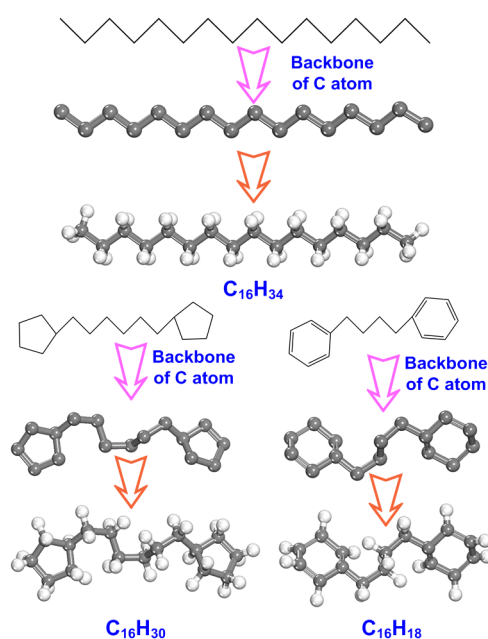


Figure 2. Main components of paraffin-based transformer oil.

1.2.1. Suitable Density

When a transformer operates at extremely low temperature, liquid water will be generated when any ice melts, and the breakdown voltage will be markedly lowered if liquid water flows into the electrode region, so the emergence of floating ice should be prevented as much as possible. Data have shown that the actual density of pure ice changes within the range of 880–920 kg/m³ at 0 °C and 0.1 MPa [10], therefore, the large difference between densities of the transformer oil and floating ice can readily control the emergence of ice. The density of paraffinic oil is lower than that of naphthenic oil at 0 and 20 °C [3], so paraffinic-based oil is more effective at controlling the emergence of floating ice than naphthenic-based oil.

1.2.2. Favorable Electrical Properties

Electrical performance is an important performance index of transformer oil, and mainly includes the breakdown voltage and dielectric loss. These two parameters are mostly affected by the moisture content of the transformer oil, because even a small amount of moisture strongly influences the breakdown voltage and dielectric loss. The breakdown voltages and dielectric losses of paraffinic-based and naphthenic-based oils are almost identical, and there is no obvious difference between their electrical properties under anhydrous conditions [3,11].

1.2.3. High Antioxidation Stability

Antioxidation stability is an important parameter reflecting the oxidation resistance of transformer oil. The antioxidation stability of paraffinic-based oil is higher than that of naphthenic-based oil [3,12], which means that paraffinic-based oil has a longer service life during long-term operation than naphthenic-based oil.

The density and antioxidation stability of paraffin-based transformer oil are better than those of naphthenic-based transformer oil. However, the solubility, low-temperature performance, and kinematic viscosity of naphthenic-based transformer oil are better than those of paraffin-based transformer oil. Meanwhile, there is little difference between the electrical properties of both oil types. Overall, these two kinds of transformer oil have their own advantages and disadvantages. However, naphthenic-based oil has superior low-temperature properties, a reasonable proportion of alkanes, cycloalkanes, and arenes, low wax content (generally below 3%), and a complex, expensive dewaxing process is not required. Thus, transformer insulating oil [3] has mainly been refined from naphthenic-based crude oil.

In 2014, the State Grid Corporation of China started the ultra-high voltage (UHV) projects with four alternating current (AC) lines and six direct current (DC) lines (ten lines in all) with a total investment of RMB 220 billion Yuan (about 35 billion US dollars) and total length of 16,000 km. This project passes through 16 provinces and creates a new record in the history of global power construction. China, along with the rest of the world, is rapidly entering a UHV era. As the properties of insulating oil and its aging by-product were proved to have close relation to the operation life of power transformers [13–17]. The continuous rise of the voltage level of power grids and continuous increase of loads mean that insulating materials now face unprecedented challenges.

Therefore, for power transformer oil to meet the insulation performance requirements for UHV power transmission, scholars all over the globe are conducting numerous studies on the modification of transformer insulating oil. In this review, studies of naphthenic mineral insulating oil for power transformers conducted in recent decades are analyzed, and some perspectives on the new developments of mineral insulating oil are discussed.

2. Properties of Mineral Insulating Oil

In a mineral oil-immersed transformer, the insulation system of the transformer consists of mineral insulating oil and insulating paper. In normal operation of such a transformer, the oil-paper

insulation system can be influenced by factors such as the electric field, thermal field, and force field. The physicochemical properties of the oil-paper insulation system gradually deteriorate over time. Therefore, these parameters can directly reflect the electrical properties of mineral insulating oil, such as the breakdown strength, dielectric constant, and conductivity. The changes of the above parameters of mineral insulating oil during operation of the transformer are analyzed in this section.

2.1. Breakdown Voltage of Mineral Insulating Oil

The electrical properties and thermal stability of insulating materials are closely correlated, and the electrical properties will deteriorate as the thermal stability of the insulating material decreases. Therefore, it is necessary to study the thermal stability of oil-paper insulation when researching its breakdown voltage. Moisture and temperature both strongly influence the aging process of the oil-paper insulation of transformers. Moisture severely affects the electrical properties of oil-paper insulation, accelerating its aging and shortening its service life [18–20].

For years, a large number of scholars have investigated the formation pathway of water in transformers and its influence on transformer performance. There are basically three states of moisture in insulating liquids, which are the dissolved state, emulsified state, and dispersed state. The moisture content in insulating oil can largely influence the electrical properties, that is, increase the electrical conductivity and dissipation factor and lower the electric strength of transformer oil [21].

In 2004, Liu [22] studied the source of moisture in the transformer, evaluated the amount of water generated through aging of the oil-paper insulation system, and derived a mathematical expression for the relationship between the aging life and moisture content of oil-paper insulation. Chen [23] developed an online calculation model to monitor the moisture content of mineral insulating oil based on the neural network for online monitoring. This model can be used to determine not only the change of the moisture content of the transformer, but also can obtain the cause of abnormal changes of moisture content of mineral insulating oil.

In 2005, Yang [24] researched the identification of the aging degree of oil-paper insulating materials by multivariate analysis of the statistics for diagnosis of the aging of oil-paper insulation. The aging characteristics were measured, such as the degree of polymerization of insulation paper, furfural content of oil, CO and CO₂ contents of mineral insulating oil, acid value of mineral insulating oil, and moisture content. The aging properties of different insulation combinations were systematically compared and analyzed, and the correlation between the aging results for different insulating materials were explored. This research showed that the insulation state of new samples can be reasonably judged using the discrimination function.

In 2012, Liao [25] studied the effect of water on the thermal aging rate and characteristic parameters of mineral oil-paper insulation. It was found that the moisture content and its variation affected the furfural and acid contents in the insulation during the aging process. These results indicated that the influence of water should be taken into account in the condition assessment and fault diagnosis of mineral oil-paper insulation according to the traditional aging characteristic parameters of oil, such as furfural and acid content.

Temperature and moisture synergistically act on the mineral oil-paper insulation system of a transformer. Zhou et al. [26] derived an equation for moisture diffusion in mineral oil-paper insulation considering Fick's second law of diffusion, and established relevant models to characterize the relationship between the aging state of mineral oil-paper insulation and the moisture content. They then studied the effect of various moisture contents on mineral oil-paper insulation at different temperatures. Distribution curves of the change of the moisture concentration with the thickness of the insulating paper at different times were measured, and the average moisture concentration in insulation paper was obtained through an integral computation of these distribution curves. The relationship between the breakdown voltage and water content of mineral insulating oil is shown in Figure 3.

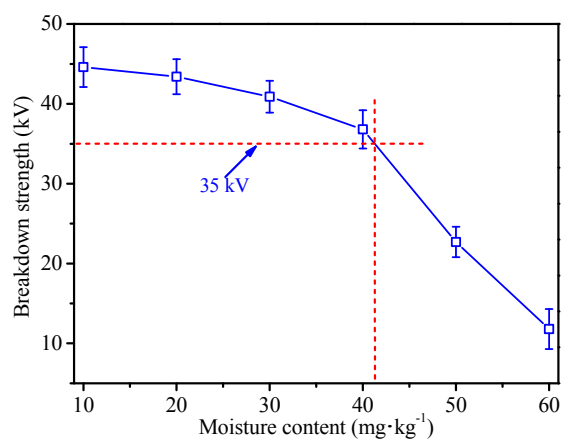


Figure 3. Relationship between the breakdown strength and moisture content of mineral insulating oil.

The thermal aging rate of mineral oil-paper insulation with different temperatures and moisture contents has been studied [25]. A strong positive correlation was found for the fluctuation amplitudes of moisture in oil and moisture in paper, and the relationship between overall fluctuation trends of these two parameters was consistent with the initial moisture content. The moisture content and its changes can affect the variation of the contents of furfural, acid, and other products during aging. When accelerated thermal aging was carried out for oil-paper insulation samples at different temperatures, it was found that the oil type was the main factor affecting the moisture content of the mineral oil.

When the mineral oil-paper insulation system is affected by moisture, the insulating material will degrade over time, the dielectric loss of the oil paper will be increased, the insulation resistance will be lowered, and the operation life of the equipment will be seriously affected. As the moisture content of mineral oil increases, its breakdown voltage rapidly decreases. Over time, the breakdown voltage of the insulating oil will lower, and especially after medium-term aging, the rate of the breakdown voltage decrease accelerates [27–33].

The power frequency breakdown voltage of the Karamay No. 25 transformer oil from the China Petroleum Chemical Co. was tested according to a standard insulation oil breakdown voltage measurement method [34]. This test revealed that the breakdown voltage of No. 25 transformer oil decreased obviously with increasing water content of the transformer oil. When the water content was more than 40 mg/kg, the breakdown voltage of the Karamay No. 25 transformer oil was close to 35 kV, which is the minimum national standard requirement for transformer oil in China.

Besides moisture, the acid generated during aging of insulating paper will enter into the insulating oil, and affect its properties. The acid has a negative influence on the safe operation of the transformer. The acid in the transformer oil may erode the metal parts in the transformer, and then the new material generated can accelerate the oxidation of the insulating oil [35,36].

Research has shown that oil type is the main factor affecting the acid content during oil aging, and the acid content of a mixture of vegetable and mineral oils is greater than that of ordinary transformer oil. When plenty of acid and water have accumulated in an insulation system, a synergistic effect of acid and water accelerates the aging of mineral oil-paper insulation. The accelerated aging effect of the acid on the insulating paper is more obvious for acids with lower molecular weight. Therefore, the acid content of the mineral oil-paper insulation is an important indicator to judge whether the operation status of a transformer is normal or not.

Based on the above analysis, on one hand, the properties of mineral insulating oil are degraded through oxidative degradation over time. On the other hand, moisture, small acid molecules, and gases like CO and CO₂ generated during thermal aging of the insulating paper will enter the mineral insulating oil [37–40]. The structures of water, gas, and acid dissolved in the oil are shown in Figure 4. Moisture and impurities in the oil can form a “small bridge” in a certain direction under the action of the electric field. When the positive and negative electrodes are connected with the small bridge,

the leakage current flowing through the small bridge will increase because of the high electrical conductivity of water and impurities, which will lead to local overheating, vaporization of water, and formation of air bubbles. Gases have lower relative dielectric constants and higher withstand voltages than those of liquids, so electrical discharge will occur first in the gas in air bubbles. More gas will be decomposed when the charged particles collide with the oil molecules, the bubble volume will continue to increase, and the bubbles will be arranged to form small air bridges that connect the electrodes under the action of an electric field. Oil breakdown occurs at the moment when the bridge breaks through both electrodes [41–43].

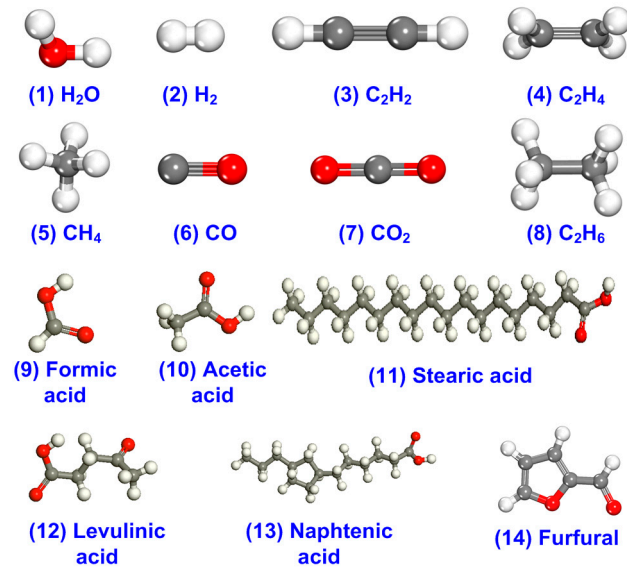


Figure 4. The water, gases, acids, etc. dissolved in mineral insulating oil of transformer.

2.2. Dielectric Constant of Mineral Insulating Oil

During the actual operation of mineral insulating oil, the molecules of the mineral insulating oil undergo physical and chemical reactions because of the influence of light, electricity, and magnetism, to form a series of products, which strongly affect the dielectric properties of the mineral insulating oil. Experiments using the return voltage measurement method [44], depolarizing current method [45,46], and frequency domain dielectric spectroscopy [47–49] have revealed that the free radical chain reaction process of autoxidation will occur in the mineral insulating oil during aging, which increases the acid content of the mineral insulating oil. Resinous substances, oligomers, and viscous substances with high molecular weight will be generated through further condensation reactions between acid and alcohol species. The moisture content will increase with the amount of compounds generated by this process, eventually leading to increased contents of oxides, alcohols, aldehydes, ketones, and acidic compounds along with water. These species intensify intermolecular thermal motion; increase the number of equivalent dipoles; disconnect molecular chains; weaken the cross-linking force; increase the polarization capacity of mineral insulating oil [50]; increase kinematic viscosity, dielectric constant, and the dielectric dissipation factor, and decrease recovery voltage. The change of these parameters affects the dielectric properties of the mineral insulating oil.

Zhou et al. [51] developed a modified Coelho model, which introduced the current density in the external circuit to modify the space charge polarization theory of Coelho. It brings a better understanding of the low-frequency response in mineral insulating oil. It can also be used to explain the dielectric behavior of traditional mineral insulating oil.

2.3. Electrical Conductivity of Mineral Insulating Oil

Zaengl [52] and Saha [53] conducted the first research on the electrical conductivity of mineral insulating oil. Their tests showed that the higher the electrical conductivity of mineral insulating oil, the higher the initial value of polarization current, and the lower the electrical conductivity of mineral insulating oil, the smaller the initial current value, which can considerably prolong the current time decayed by index. In 2010, Ma [54] and Yang [55] measured the DC electrical conductivity of mineral insulating oil at 90 °C according to the standard 'Determination of Volume Resistivity of Power Oils' [56]. They found that the DC electrical conductivity of the mineral insulating oil gradually increased during the aging process. According to their analysis, this was caused by the dissolution of the organic acids and other substances generated through oxidative degradation of the mineral insulating oil during the aging process. By analyzing the change of the acid content of mineral insulating oil, Hao [49] concluded that an increased acid content of mineral insulating oil will raise the electrical conductivity of oil products and decrease the insulation properties of the oil. During aging, if the acid content of mineral insulating oil gradually increases, the electrical conductivity also rises, especially during the later stage of aging. A large number of reports indicate that the conductivity of oil increases during the aging of mineral oil-paper insulation [49,54–57].

Zhou and co-workers suggested to the characterize charge carriers in mineral insulating oil by using the polarization and depolarization currents, and simulate the frequency response by the calculated insulating oil conductivity [58,59].

The increase of the electrical conductivity of mineral insulating oil over time is mainly caused by the increasing content of aging products dissolved in the mineral insulating oil, such as water, acid, and furan compounds, during aging [60]. In addition, small particles, such as electrically insulating particles (silica and paper), semiconducting particles (carbon), and conducting particles (copper), have been found to have a direct relationship with the electrical conductivity of mineral insulating oil [61–63]. For example, semiconducting particles such as carbon led to markedly increased conductivity.

Our team measured the relationship between the acid content of mineral insulating oil and electrical conductivity of the mineral oil-paper insulating system. The experimental samples were composed of No. 25 transformer oil produced in Karamay, Xinjiang, and the insulation winding was provided by Chongqing ABB Transformer Co., Ltd. (Chongqing, China) Both sides of the copper strip of the winding were covered with ten layers of cellulose insulating paper with a thickness of 75 µm, and the length and width of the winding were 12 and 2.8 cm, respectively.

The results of the experiment are presented in Figure 5. During the aging process of the mineral oil-paper insulating system, the oleic acid content and electrical conductivity of the mineral insulating oil increased, especially during the later stage of aging. The increase of the acid content of mineral insulating oil will raise its conductivity and degrade its insulation performance.

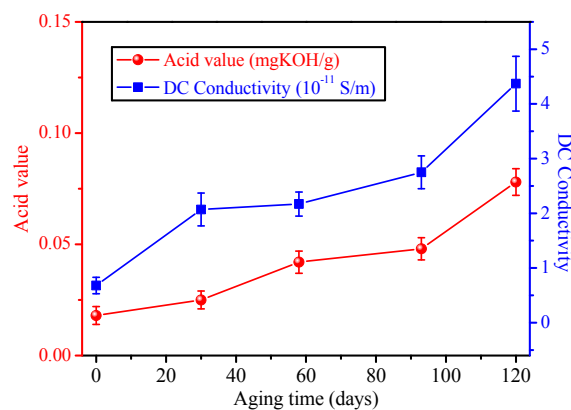


Figure 5. Relationships between the acid value, DC conductivity, and aging time of mineral insulating oil.

3. Modification of Mineral Insulating Oil

The above analysis reveals that temperature, moisture, and small acid molecules are the most important factors affecting the electrical performance of mineral insulating oil. Next, methods to improve the performance of mineral insulating oil based on the main factors leading to the decrease of the properties of mineral insulating oil are introduced.

3.1. Modification with Nanoparticles

In 1994, the concept of a “nano-dielectric” was proposed by Lewis [64], which considers that the properties of nanoscale dielectrics are determined by the interface between the nanoscale dielectric and substrate material. The interface effect is an important characteristic of a nanoscale dielectric that determines its electrical properties. In 1995, the concept of nanofluids was proposed by Choi [65]. Nanoscale additives do not easily settle in a liquid medium, their surface area is large, and their thermal conductivity is high. As a result, these studies opened a new chapter in the modification of mineral insulating oil. Nanoparticles are now widely used to modify mineral insulating oil and represent a new type of material.

3.1.1. Effect of Nanoparticles on the Breakdown Voltage of Mineral Insulating Oil

The decrease of the breakdown voltage is one of the most prominent problems during the aging of mineral insulating oil. Dariusz and Aksamit [66,67] modified new and aged mineral insulating oil with fullerene (C_{60}) (Figure 6), and then measured the breakdown voltage of the modified mineral insulating oil samples. They found that the dielectric loss of the modified oil was lower, and its breakdown voltage remained higher during the aging process.

The water content measurements of the mineral insulating oil samples showed that all the C_{60} -doped samples had lower water contents than those of the samples without added C_{60} . With increasing C_{60} content, the water absorption by the mineral insulating oil samples decreased.

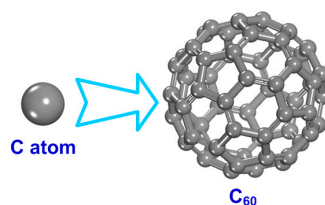


Figure 6. Molecular structure of fullerene (C_{60}).

Prasath et al. [68] modified mineral insulating oil with $CaCu_3Ti_4O_{12}$ (CCTO) nanoparticles, which have a high dielectric constant. Nano-fluids containing mineral oils with of different CCTO contents were prepared using the ultrasonic effect. Important parameters of these nanomaterial-modified mineral insulating oil samples (also called nanofluids) were measured according to the procedures of ASTM (American Society for Testing and Materials) and IEC (International Electrotechnical Commission) standards. The results showed that the AC breakdown voltage increased with the content of CCTO nanoparticles in the mineral insulating oil. The breakdown voltages of mineral insulating oil modified with C_{60} and CCTO nanoparticles are listed in Table 1.

As a semiconductor material, nano- TiO_2 is widely used in the modified mineral insulating oil, thereby increasing the breakdown voltage of the mineral insulating oil, and the molecular model of nano- TiO_2 is shown in Figure 7. When the mineral insulating oil is modified the nano- TiO_2 of the content 1% [69], the value of breakdown voltage of nano-modified mineral insulating oil rises by 1.15 and 1.43 times. For the lightning breakdown voltage, the nano-modified oil was 13.3 kV higher than that of the mineral insulating oil. On this basis, the surfaces of the nano- TiO_2 shall be modified with octadecanoic acid [70], and then added into the mineral insulating oil, which can improve the dielectrical property of insulating oil and the breakdown voltage in AC state.

Table 1. Breakdown voltages of mineral insulation oil modified with C₆₀ and CCTO.

Nanoparticles	Year, Author	Manufacture Factory, Modified Object	Measurement Standard	Optimal Nanoparticles Concentration	Breakdown Voltage (kV)
C ₆₀	2014, Dariusz Z, et al. [66,67]	ORLEN OIL TRAF, fresh uninhibited mineral oil	AC, IEC 60156, spherical spark gap, 2.5 mm gap	250 mg/L 150 mg/L 300 mg/L	About 77 (aged at 110 °C, 0 h) About 67 (aged at 110 °C, 48 h) About 56 (aged at 110 °C, 144 h)
CaCu ₃ Ti ₄ O ₁₂ (CCTO)	2017, Prasath RTAR, et al. [68]	Local manufacturers, mineral oil	AC, IEC 60156, spherical electrode, 2.5 mm gap	0.01% (volume fractions) 0.005% (volume fractions)	46.4 (unaged) 36.7 (ageing based on ASTM D1934)

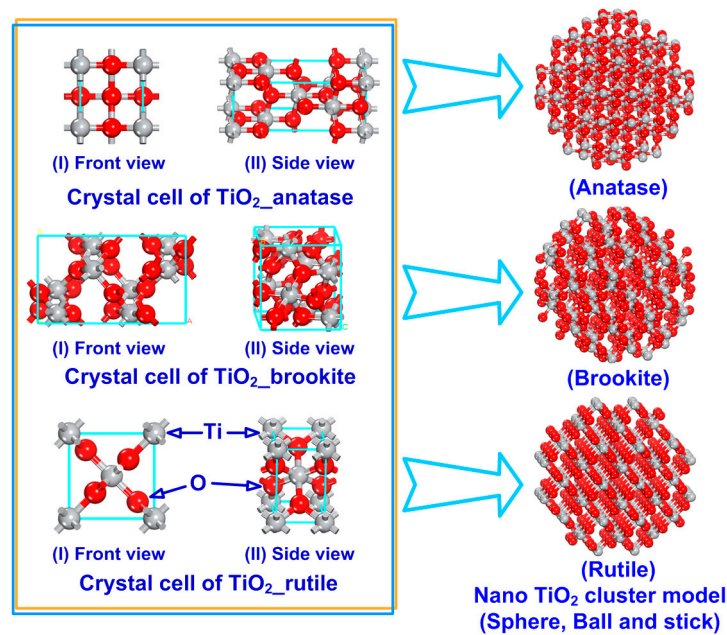


Figure 7. The molecular model of nano-TiO₂.

Wang and Raffia [71] modified mineral insulating oil with 5–40 wt % nano-TiO₂, and measured the impulse breakdown voltage of the oil samples before and after modification according to an IEC standard. Under positive pulse conditions, at a certain concentration, the breakdown strength increased to the maximum value firstly, and then, it began to decrease. Under negative pulse conditions, the breakdown voltage of the samples with different nano-TiO₂ concentrations was lower than that of the unmodified mineral insulating oil. This indicates that when the content of nanoparticles is too high, they will aggregate in the mineral insulating oil, which causes degradation of performance.

The mechanism behind the breakdown voltage increase of mineral insulating oil after nano-TiO₂ modification is that the polarization of nano-TiO₂ acts as an electronic trap in the electron transfer process of electrically stressed nanofluids. In addition, the high specific surface area of the nanoparticles have the effects of increasing the possibility of electron scattering, lowering the electronic impact energy, and preventing oil ionization. The oil diffusion behavior and trap network are changed by the addition of nano-TiO₂, effectively lowering the mobility of carriers.

Du et al. [72] also studied the effect of nano-TiO₂ on the aging performance of the mineral insulating oil. They carried out accelerated aging testing of unmodified and nano-TiO₂-modified mineral insulating oil samples for 6 days, measuring the dielectric breakdown voltage and partial discharge inception voltage of the samples. The partial discharge inception voltage of the modified mineral insulating oil was 1.16 times that of the unmodified mineral insulating oil after aging, and the breakdown voltage was up to 8 kV higher than that of the unmodified mineral insulating oil. These results show that the dielectric breakdown voltage and partial discharge inception voltage of mineral insulating oil can be effectively improved by modification with nano-TiO₂. The above studies illustrate that nano-TiO₂ has a positive effect on the breakdown voltage of the mineral insulating oil.

SiO₂ nanoparticles (denoted nano-SiO₂), as shown in Figure 8, are also often used as insulating nanoparticles to modify insulating oil. Muhammad and Li [73] added nano-SiO₂ to Karamay No. 25 mineral oil to give a volume fraction of nano-SiO₂ of 20%. Their measurement results showed that the AC breakdown voltage of the nano-SiO₂-modified insulating oil was higher than that of the unmodified mineral insulating oil, but the breakdown voltage decreased as the humidity of samples increased.

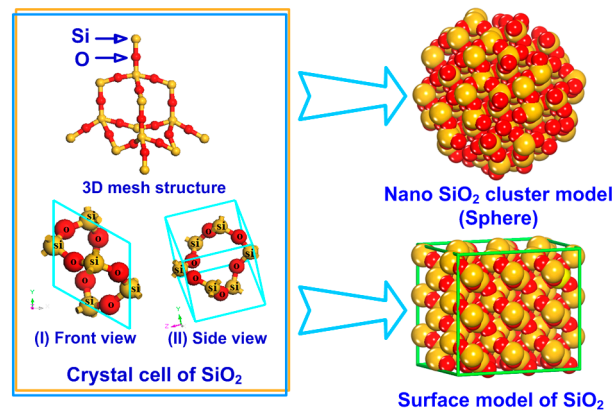


Figure 8. The molecular model of nano-SiO₂.

Ma et al. [74] added 1 wt % nano-SiO₂ to mineral insulating oil. The sample was aged of 35 days at 100 °C, and parameter testing was carried out every 7 days. They found that the addition of nano-SiO₂ increased the breakdown voltage of mineral insulating oil during the aging process. The breakdown voltages of mineral insulating oil modified with nano-SiO₂ and nano-TiO₂ are presented in Table 2.

Similarly, Al₂O₃ has been widely studied as an insulating nanomaterial. Ajay and Purbarun [75] added Al₂O₃ particles with a size of 25–125 nm to mineral insulating oil. The effects of the concentration, morphology, permittivity, and size of the nanoparticles on the breakdown characteristics of the modified oil were studied.

For nonconductive nano-Al₂O₃, the polarization of the dielectric nanoparticles will produce a potential trap under the influence of an external electric field, which slows down the fast-moving electrons and converts them to negatively charged nanoparticles. Moreover, the higher mobility of electrons will lead to the greater shielding effect of nanoparticles.

The performance of nano-Al₂O₃-modified insulating oil has been measured with different electrode materials [76]. It was found that the breakdown voltage of nano-Al₂O₃-modified mineral insulating oil was higher than that of the unmodified mineral insulating oil. The maximum breakdown voltage was observed when concentration of nano-Al₂O₃ was 20 mg/L. The molecular structure of nano-Al₂O₃ is depicted in Figure 9.

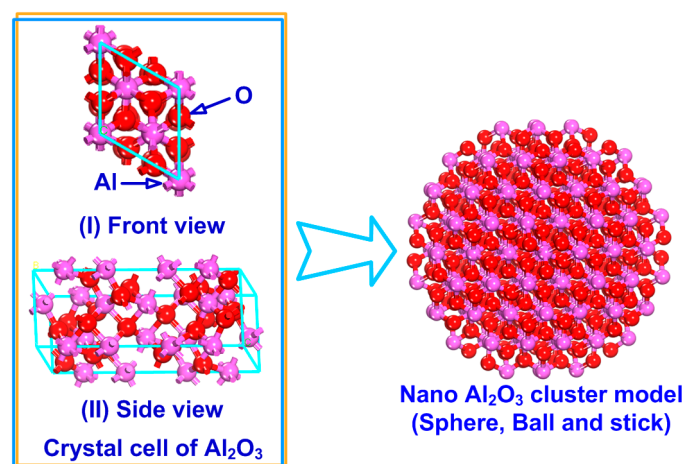


Figure 9. Molecular structure of nano-Al₂O₃.

Table 2. Breakdown voltages of mineral insulating oil modified with nano-TiO₂ and nano-SiO₂.

Nano-Particles	Year, Author	Manufacture Factory, Modified Object	Measurement Standard	Optimal Nanoparticles Concentration	Breakdown Voltage (kV)
TiO ₂	2010, Du Y F, et al. [69]	Mineral oil	AC, IEC 60156, brass spherical electrodes, 2.5 mm gap	0.01 mg/L	57.8
	2011, Du Y F, et al. [70]	Mineral oil	AC, IEC60156, brass spherical electrodes, 2.5 mm gap	0.006 g/L	82.48
	2011, Du Y F, et al. [72]	Filtered mineral oil	AC, IEC60156, brass spherically-capped electrodes, 2 mm gap	0.075% (volume fractions)	80.9 (aged at 130 °C, 6 days)
	2016, Wang Q, et al. [71]	Petro China, No. 25 Kelamayi, filtered mineral oil	Impulse breakdown, IEC 60897, needle sphere electrode, 25 mm gap	10% <i>w/v</i>	About 78 (Positive impulse breakdown)
SiO ₂	2016, Rafiq M, et al. [73]	Petro China, No. 25 Kelamayi, filtered mineral oil	AC, IEC 60897, brass spherical electrodes, 2 mm gap	20% (volume fractions)	About 76
	2016, Jun M, et al. [74]	Petro China, No. 25 Kelamayi, mineral oil	GB/T 507—2002	1 wt %	63.0 (110 °C, 0 day) 54.1 (110 °C, 14 days) 38.5 (110 °C, 35 days)

The average AC breakdown voltage of the Fe_3O_4 nanoparticle (nano- Fe_3O_4)-modified mineral insulating oil with an optimal nano- Fe_3O_4 concentration is 1.26 times that of the unmodified oil [77], and its average lightning breakdown voltage is 24% higher than that of the unmodified mineral insulating oil. The performance of the natural ester and nano- Fe_3O_4 -modified mineral insulating oil was compared [78]. The experimental results showed that the nano- Fe_3O_4 -modified mineral oil exhibited better performance than a mixture of natural esters and mineral oil from the aspects of dielectric properties and breakdown voltage. Therefore, nanofluids are considered as potential alternatives to conventional dielectric fluids. The breakdown voltage parameters of mineral insulating oil modified with nano- Fe_3O_4 and nano- Al_2O_3 are shown in Table 3. The molecular structure of nano- Fe_3O_4 particles is illustrated in Figure 10.

The above studies show that the addition of nanomaterials to mineral insulating oil can effectively increase its breakdown voltage. The mechanism behind this effect has been analyzed from the angle of microelectronics. Most researchers believe that the interfacial characteristics between the mineral insulating oil and nanoparticles play a dominant role in the space-charge transport during the breakdown process in nanofluids [73]. The oil–nanoparticle interface contains a large number of electronic traps, which repeatedly capture and release electrons. Such trapping lowers the electron mobility and energy transformation, and hinders the further development of the streamer in the electron capture and release process. In addition, both positive and negative pulse penetration tests have revealed that the addition of nanoparticles increases the positive and negative pulse penetration voltage of mineral insulating oil. The nanoparticles can absorb impurities in the mineral insulating oil, which suppresses the bridging effect and increases the breakdown voltage of the mineral insulating oil.

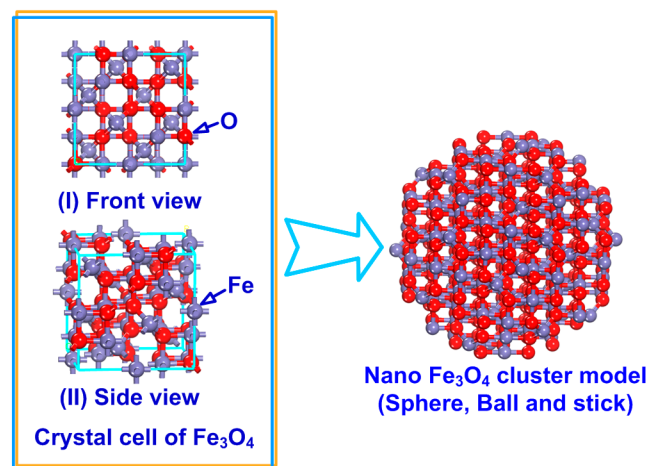


Figure 10. Molecular structure of nano- Fe_3O_4 .

Table 3. Breakdown voltages of nano-Al₂O₃-modified and nano-Fe₃O₄-modified mineral insulating oils.

Nano-Particles	Year, Author	Manufacture Factory, Modified Object	Measurement Standard	Optimal Nanoparticles Concentration	Breakdown Voltage (kV)
Al ₂ O ₃	2016, Katiyar A, et al. [75]	Mineral oil	AC, ASTM D-877, hemispherical electrodes, 5 mm gap	0.25 wt % (r = 23 nm)	About 68
	2016, Wang Q, et al. [71]	Petro China, No. 25 Kelamayi, filtered mineral oil	Impulse breakdown, IEC 60897, needle sphere electrode, 25 mm gap	20% w/v	About 85 (Positive impulse breakdown)
	2017, Qing Y, et al. [76]	Petro China, No. 25 Kelamayi, filtered oil	Impulse breakdown, brass electrodes, 1 mm gap	20 mg/L	About 40 (Impulse breakdown)
Fe ₃ O ₄	2012, Zhou J Q, et al. [77]	Petro China, No. 25 Karamay, filtered mineral oil	AC, IEC 60156, brass spherical electrodes, 2.5 mm gap	1%	83.2
	2016, Wang Q, et al. [71]	Petro China, No. 25 Kelamayi, filtered mineral oil	Impulse breakdown, IEC 60897, needle sphere electrode, 25 mm gap	10% w/v	About 82 (Positive impulse breakdown)
	2016, Peppas G D, et al. [78]	Public Power Corporation of Greece, Shell Diala S2 ZU-I Filtered mineral oil	AC, IEC 60156, brass steel Rogowski electrodes, 2.5 mm gap	0.008%	About 77.7

3.1.2. Effect of Nanoparticles on the Dielectric Properties of Mineral Insulating Oil

In addition to breakdown voltage, the dielectric properties are also important parameters that reflect the electrical properties of mineral insulating oil. A study of mineral insulating oil modified with the ceramic nanomaterials zirconia (ZrO_2) and TiO_2 showed that the dielectric dissipation factor of the modified mineral insulating oil was lower than that of the unmodified mineral insulating oil [79]. Compared with the dielectric dissipation factor of nano- ZrO_2 -modified mineral insulating oil, the nano- TiO_2 -modified mineral insulating oil was higher. This may be because of the higher relative permittivity of nano- TiO_2 particles than that of nano- ZrO_2 particles. The kinematic viscosities of the nano- TiO_2 fluids were higher than those of nano- ZrO_2 because the particle size of the nano- TiO_2 fillers are larger than that of nano- ZrO_2 , so the fluid flow can be prevented more effectively. The molecular structure of nano- ZrO_2 is depicted in Figure 11.

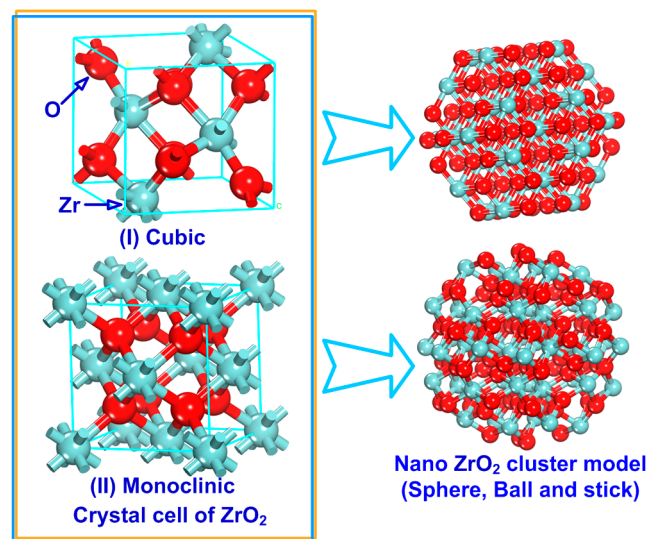


Figure 11. The molecular model of nano- ZrO_2 .

A study of nano- TiO_2 -modified DB-No 25 mineral insulating oil showed that a new low-frequency component (from 0.1 to 1 MHz) appeared in the dielectric frequency response of the nano- TiO_2 -modified oil-paper insulating materials at different temperature and moisture contents [80].

In addition to nano- TiO_2 , the improvement of the dielectric properties of mineral insulating oil induced by adding nano- SiO_2 has been investigated [81]. For these nanofluids, the dielectric withstand properties in a quasi-uniform field were enhanced when the nano- SiO_2 concentration was kept at about 0.2 g/L.

Ajay and Purbarun [75] modified mineral insulating oil with nano- Al_2O_3 with different particle sizes, and then measured the electrical parameters of the samples. The results showed that the dielectric properties increased by 69% when the content of nano- Al_2O_3 with a particle size of 23 nm was 0.25 wt %.

The above experiments reveal that the smaller the radius of the nanoparticles, the more obvious the improvement of the electrical properties of the modified mineral insulating oil. In addition, the electrical properties of modified mineral insulating oil tend to improve with increasing nanoparticle concentration.

3.1.3. Effect of Nanoparticles on the Thermal Stability of Mineral Insulating Oil

The internal temperature of a transformer during long-term operation is high. Therefore, mineral insulating oil needs to possess high thermal stability. Mineral insulating oil has been modified through the addition of boron nitride nanoparticles (nano-BN), as shown in Figure 12, to raise its thermal

stability [82]. It was found that the thermal stability of the mineral oil modified with nano-BN was higher than that of the unmodified mineral insulating oil. When the nano-BN content was 0.1 wt %, the thermal conductivity of the modified oil increased continuously with rising temperature, and the increase was more than 70% when the temperature reached 27 °C.

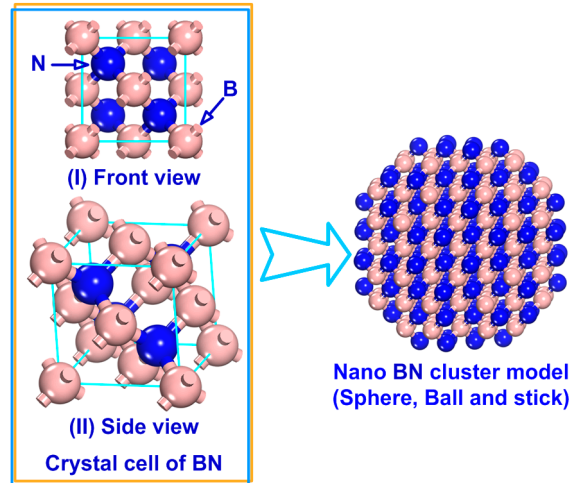


Figure 12. The molecular model of nano-BN.

Modification of mineral insulating oil with nanodiamond (ND) and subsequent measurements revealed that the thermal conductivity of the mineral insulating oil modified with a ND mass fraction of 0.12% was 14.5% higher than that of the unmodified insulating oil [83]. The change in the viscosity of the base fluid with a ND loading of up to 1% was quite small. It is noteworthy that greater enhancements of the thermal conductivity can be achieved by designing the ND covalent surface modifications, and optimizing the ND/base fluid solvation.

Cadena-dela et al. [84] studied the thermal properties of mineral oil-based nanofluids containing dispersed aluminum nitride nanoparticles (nano-AlN) and nano-TiO₂. Their results indicated that the thermal transfer coefficient of mineral insulating oil can be improved and the internal heat of the transformer can be easily dissipated through the addition of nanoparticles. When the nano-TiO₂ content was 0.01 wt %, the kinematic viscosity was the lowest (15.80 m²/s at 24 °C). A nano-AlN content of 0.01 wt % gave the lowest kinematic viscosity of 15.82 m²/s at 24 °C. At 40 °C, the same nano-TiO₂ and nano-AlN-modified samples displayed lowest kinematic viscosities of 7.21 and 7.32 m²/s, respectively. In general, the viscosity of mineral insulating oil modified with nano-TiO₂ was lower than that with nano-AlN, and nano-TiO₂ also improved the thermal stability of the mineral insulating oil more than nano-AlN.

When Lv et al. [85] added nano-TiO₂ to mineral insulating oil, they found that the diameter of impurities was decreased, and the sample fluidity under a low electric field was greatly improved. The charged nanoparticles became the major transmission factors and slowly floated with increasing electrical stress because the mineral insulating molecules provided high viscous resistance.

The above analysis illustrates that the modification of mineral insulating oil with nanomaterials can obviously enhance the three properties of power frequency breakdown, partial discharge voltage, and positive impulse breakdown voltage. The strengthening the negative-polarity impulse breakdown voltage is affected by the surface modification method of nanoparticles, original oil samples, and testing method. Analysis has revealed that the addition of nanoparticles will decrease the resistivity of mineral insulating oil and increase its dielectric loss angle [86]. Typical dielectric properties of mineral insulating oil and nanofluids are listed in Table 4.

Table 4. Typical dielectric properties of mineral insulating oil and nanofluids.

Oils	Resistivity ($\Omega \cdot m$)	$\tan \delta$	Relative Permittivity (ϵ_r)
Pure oil	1.41×10^{12}	0.008	2.19
Fe ₃ O ₄ nanofluids	2.05×10^{10}	0.360	2.35
TiO ₂ nanofluids	2.53×10^{10}	0.488	2.90
Al ₂ O ₃ nanofluids	2.56×10^{11}	0.046	2.27

3.2. Modification of Non-Nanoparticles

The limited availability of petroleum resources and increasingly serious environmental problems drive the search for alternatives to mineral insulating oil. Natural esters are considered an attractive green alternative to mineral insulating oil [1,87], and mixtures composed of natural esters and mineral insulating oil have become a research interest. In 2002, Fofana et al. [21] studied the electrical and physicochemical properties of mixtures of natural esters and mineral insulating oil with different proportions. They found that when the natural ester content was less than 20%, all the electrical and physical properties of the mixtures were better than those of the traditional transformer mineral insulating oil. When the ester content exceeded 50%, the density and viscosity exceeded the standard limits. During determination of the mass of mineral insulating oil, the density is generally not important; however, it does become important at lower temperature. Addition of natural esters to mineral insulating oil helps to suppress gasification under local thermal stress. In 2009, Liao et al. [30] found that natural esters display high water saturation, and can help to restrain oxidation reactions of the mixed oil when added to mineral insulating oil. However, the viscosity of natural esters is high, so an excessive content of natural esters will enhance the viscosity of the mixed oil. This conclusion is consistent with the results of Fofana et al. [21], who also researched the electrical, physicochemical, and degradation properties of mixtures of mineral insulating oil with natural esters (olive oil) with different components. They found that hydrolysis of the natural esters increased the acid content of the mineral insulating oil and decreased the breakdown voltage of the mixed oil. The oxidation stability of mineral insulating oil can be effectively improved by using an appropriate proportion of natural esters to mineral insulating oil and adding an antioxidant.

Test results have indicated that the biodegradability of mixed insulating oils is higher than that of mineral insulating oil and more environmentally benign. For example, Yusrnida et al. [88] added palm oil to mineral insulating oil and researched the breakdown characteristics of the mixtures with different contents of palm oil. It was found that when the content of palm oil was less than 20%, the breakdown strength of the mixed oil decreased with increasing palm oil content. When the palm oil content was more than 20%, the breakdown strength of mixed oil increased with the palm oil content. When the content of palm oil was 80%, the maximum breakdown strength of 87 kV was observed. Moreover, the kinematic viscosity of the mixed oil at 40 °C rose with increasing palm oil content.

Rapp et al. [89] found that natural esters have a high affinity for water, and will allow more water to be transferred from the cellulose paper to the natural ester liquid. At the same time, the natural esters will consume the moisture in the fluid through hydrolysis and allow the moisture to reach a steady dynamic equilibrium between the cellulose paper and esters. However, free fatty acids are produced as secondary reactants of ester exchange reactions during the hydrolysis, which can change the structure of cellulose and degrade the electrical properties of the cellulose paper. In 2010, Liao et al. [90] found that the anti-aging ability of mixed oil-paper insulation with natural esters added to the mineral insulating oil was superior to that of mineral oil-paper insulation. The reason for this is that the natural esters in the mixed oil-paper insulation form stable hydrogen bonds with moisture and acid molecules, and weaken the synergistic hazardous effect of moisture and acid on the insulating paper. At the same time, the esterification of hydroxyl and fatty acids in insulating paper cellulose can inhibit the aging of the insulation paper [91]. In addition, the thermal cracking rate of the mixed oil-paper insulation was lower than that of mineral insulating oil-paper insulation.

In 2011, Liao et al. [92] pointed out that the main reason for the considerable inhibitory effect of mixed oil on the aging rate of oil-paper insulation is that the aged insulation paper generates new ester groups. These ester groups inhibit insulating paper thermal aging. The content of aldehyde groups generated during aging of mixed oil-paper insulation is lower than that generated in the mineral oil-paper insulation. It was found that the mixed oil can restrain its own oxidation and the degradation rate of the insulating paper, and also improve the thermal stability of mineral insulating oil-paper insulation systems [93]. Studies on the thermal aging of mixed oils with natural esters have revealed that the water and acid values of the mixed oil-paper insulation are higher than those of the mineral insulating oil-paper insulation, and the mixed oil-paper insulation has a higher breakdown voltage than that of the mineral oil-paper insulation [94].

In summary, natural esters possess the advantages of high flash point and ignition point, good electrical properties, high biodegradability, and high abundance and have thus been widely used as insulating materials. However, the kinematic viscosity of most natural ester fluids is high, which will adversely affect the heat emission of a transformer when used as insulating oil. In addition, the acid content of natural esters after aging is higher than that of traditional mineral insulating oil, affecting the performance of mineral insulating oil-paper insulation. When natural esters are added to mineral insulating oil, the natural esters and the aged insulation paper undergo chemical reactions to form ester groups, and restrain the aging of the oil-paper insulation system and prolongs the service life of the mineral insulating oil-paper insulation. Therefore, the appropriate proportions of mineral insulating oil and natural esters can realize mixed oils that possess the complementary advantages of both materials.

4. Application of Computer Simulation Technology

In 1901, Gibbs introduced the concept of an ensemble [95], which led to a big step forward in molecular calculations based on statistical mechanics. In 1947, the creation of electronic computers made large-scale scientific calculation possible. Since then, computational molecular science has developed rapidly and is now widely used in many fields, like chemical engineering, material engineering, pharmaceutical engineering, and life sciences, because of its great potential and strength [96]. Computer-based molecular simulations are usually conducted by one of two methods: the Monte Carlo method (MC) [97] or the molecular dynamics (MD) method [98], although quantum mechanics and molecular mechanics methods also exist [99–103]. Although there has been almost no change of the central algorithm of molecular simulation since the 1950s, the constant update of optimization algorithms means that the efficiency of molecular simulation is continuously improving.

The dynamic properties simulated by MD calculations have been widely used in materials and life sciences. The interaction modes and energies of molecules, atoms, or ions; energy components like bond energy and angle energy; gyration radius; tension; pressure; volume; and cell parameters can be calculated for multimolecular, macromolecular, and solution systems. Through the analysis of MD calculation results, the radial distribution function (RDF), mean square displacement (MSD) and fluctuation analysis results can be obtained. As a result, the stacking properties, orientation, compression properties, and phase transition properties of materials and systems can be acquired.

In recent years, the concept of high-voltage engineering calculations has been developed. In this research category, the quantitative analytical techniques used in many interdisciplinary subjects including electrical science, quantum mechanics, material physics, and computational chemistry are integrated. Numerical simulation and analysis can be carried out to investigate scientific and technical problems in high voltage engineering using electronic computers and the discrete numerical method, forming new interdisciplinary branches [104].

Molecular simulation technology can provide basic methodology and quantitative analysis methods to reveal the microphysical and chemical properties of electrical insulation, resolving the insulation degradation and destruction mechanism of power equipment. According to the development status of high-voltage and insulation technology, the computer simulation methods of multiphysics

numerical simulation and electromagnetic transient analysis are combined to achieve effective theoretical support for high-voltage engineering practice. In recent years, great success has been obtained in the study of the performance of mineral oil-paper insulation systems at molecular and atomic levels using molecular simulation.

4.1. Molecular Simulation of Water and Acid in Oil Paper Insulation System

In 2007, Lu [105] studied the effects of water and acid on mineral oil-paper insulation systems by simulations using the Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) force field. In 2009, Liang [29] researched the anti-aging performance of transformer oil and the effect of the insulating paper on thermal aging. It was found that the ester exchange reaction between the polymer acid and cellulose in the mixed oil and hydrogen bonds generated between the ketonic oxygen atoms of the esters and water molecules provided joint anti-aging ability. The degradation rate of the insulating paper in the mixed oil was obviously slower than that of the insulating paper in mineral insulating oil. The biological degradability of environmentally friendly anti-aging transformer oil and thermal aging properties of oil-paper insulation have been researched [106]. The binding of environmentally friendly anti-aging oil with water molecules is stronger than that of mineral oil, the aging of mixed oil is obviously slower than that of mineral insulating oil, and the polymerization degree of mixed oil-impregnated insulating paper is obviously higher than that mineral oil-impregnated insulating paper.

In 2010, Liao et al. [90] investigated the effects of water and acid on thermal aging of mineral insulating oil-cellulose insulating paper and mixed oil-cellulose insulating paper. Their results showed that the anti-aging ability of the mixed oil-insulation paper was superior to that of the mineral insulating oil-paper; the natural esters in the mixed oil-paper system containing water and acid can form stable hydrogen bonds, which suppress the synergistic hazardous effect of moisture and acid on the insulating paper. In the mixed oil-paper insulation system, the esterification of hydroxyl and fatty acids in the insulating paper cellulose inhibited the aging of the insulation paper. The group found that the molecular conformations of oil on different surfaces of the cellulose were varied through analysis of the mutual interactions between the mineral insulating oil-paper insulation materials. The conformation of oil molecules and cellulose molecules at the interface of an amorphous region is shown in Figure 13. The diffusion of moisture in the paper was obstructed because of the change of mineral insulating oil density at the surface of the cellulose crystal; this phenomenon will accelerate the diffusion of moisture in the paper [107]. Then same group then researched the effect of initial moisture content on the thermal properties of mineral oil-paper insulation [108]. Their results showed that the diffusion capacity of furfural and small acid molecules obviously decreased with increasing moisture content. This is because moisture, furfural, and small acid molecules generate stable hydrogen bonds. At the same time, the interaction energy is changed because of the polarity of these species.

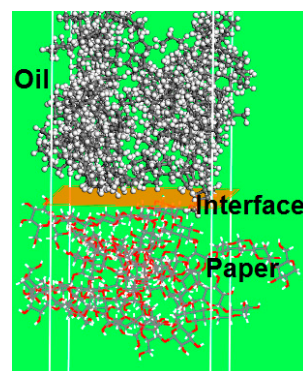


Figure 13. Simulated conformation of oil and cellulose molecules in the cellulose amorphous region at an oil-paper interface.

4.2. Molecular Simulation of Thermal Cracking

The pyrolysis of mineral insulating oil is one of its main types of degradation when internal insulation defects occur in transformers. Molecular simulation is an important tool to study microscopic mechanisms. The pyrolysis mechanism of mineral oil-paper insulation systems has been studied by molecular simulation in recent years. The results provide potential guiding value to further understand the cracking process of oil-paper insulation systems and evaluate the insulation life of the transformer after overheating defects form.

In order to research the generative mechanisms associated with the pyrolysis of triglycerides, Zhang et al. [109] carried out 500 ps MD simulations on a tripalmitin model by using a reactive force field (ReaxFF) at 1500 and 2000 K. In 2016, Zhang [110] used a molecular simulation method based on ReaxFF to study the microcosmic mechanism of the pyrolysis process of mineral oil-paper insulation, and clarified the initial cracking mechanism of the insulating paper and the formation mechanism of the main products through the mutual verification of theories and experiments; meanwhile, the micro dynamic mechanism of the thermal cracking of insulating paper was studied at the atomic level. In 2016, Lin et al. [111] studied the reaction mechanism of thermal cracking of transformer oil through molecular simulation, established a simulation model of mineral insulating oil molecules at different temperatures, and studied the generation rules of gas molecules in oil during transformer pyrolysis. The micro cracking mechanism of the three typical components of alkanes, cycloalkanes, and aromatic hydrocarbons in transformer oil was studied using ReaxFF to determine the relationship between temperature and the pyrolysis process. The proposed kinetic mechanism of thermal decomposition of mineral insulating oil at the atomic level was consistent with the pyrolysis results obtained from experiments.

In 2017, Wang et al. [4] tried to reveal the dynamic reaction mechanism at an atomic level using the ReaxFF to simulate reactive MD of mineral insulating oil pyrolysis at high temperature and the influence of acid in the mineral insulating oil on pyrolysis. It was found that as the temperature rises, the cracking rate of all three reactants considered in the paper will speed up markedly and the pyrolysis products are mainly small molecules and radicals. The reaction paths revealed that under acidic conditions, H atom is mainly produced by the reaction between hydroxyl H in formic acid and H in hydrocarbons, which is found to be the reason for the acceleration of pyrolysis of mineral insulating oil by formic acid.

4.3. Molecular Simulation of Small Molecular Diffusion

The diffusion behavior of soluble materials in mineral insulating oil (including moisture and gas molecules) and its effect on the properties of mineral oil-paper insulation has been investigated. In particular, the diffusion behavior of small molecules in oil-paper insulation has been considered [105,112,113]. The free volume theory has been proposed to explain the diffusion and mass transfer phenomenon for gas in mineral insulating oil on the basis of the diffusion of gas produced by the aging of mineral oil-paper insulation systems [105]. The free volume theory is of great important to understand the diffusion behavior of small gas molecules in mineral insulating oil. In other work, a microcosmic model of insulating paper and oil paper was created based on the molecular simulation method [112]. The movement trajectory and diffusion coefficient of moisture in this model at different temperatures was calculated through MD. The relationship between the diffusion coefficient, free volume in the model, and movement trajectory of water molecules was examined. The diffusion coefficient of the water molecules was obtained experimentally, which verified the calculation results. The results obtained by the molecular simulation were 84–222% of the values of experimental data. The microscopic mechanism of gas molecular diffusion has been analyzed through diffusion coefficients, displacement characteristics, free volumes, and interactions [114]. The differences in the diffusion characteristics of different gas molecules were discussed, and the factors that influence gas molecules diffusion were compared; these results are summarized in Tables 5 and 6 (D is the diffusion coefficient, a is the slope of the curve, R^2 is the goodness of fit). Studies show that the

diffusion coefficient of gas molecules in cellulose is lower than that in oil by one order of magnitude, and the diffusion coefficients of the gas molecules in two insulating media are of different orders. The free volume is the main factor that influences the gas diffusion behavior in oils, whereas the intermolecular interaction is the main factor that influences the diffusion behavior of celluloses.

Table 5. Diffusion coefficients of gas molecules in oil ($\text{\AA}^2/\text{s}$) [114].

Parameter	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	CO	CO ₂
<i>a</i>	10.886	1.3875	2.7873	2.2322	2.0577	3.4631	1.6641
<i>R</i> ²	0.9898	0.9640	0.9976	0.9848	0.9933	0.9729	0.9822
<i>D</i>	1.8143	0.4645	0.2773	0.3720	0.2313	0.5772	0.3429

Table 6. Diffusion coefficients of gas molecules in cellulose ($\text{\AA}^2/\text{s}$) [114].

Parameter	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	CO	CO ₂
<i>a</i>	0.3491	0.1893	0.0523	0.1297	0.1618	0.3158	0.2655
<i>R</i> ²	0.8682	0.9230	0.5049	0.7766	0.8976	0.8628	0.9601
<i>D</i>	0.0582	0.0316	0.0087	0.0216	0.0270	0.0526	0.0443

4.4. Molecular Simulation of Nanoparticle Modification

In recent years, increasing attention has been paid to the use of nanomaterials in the oil-paper insulation of transformers. Many studies have been conducted on nanoparticle modification as a method to improve the performance of mineral oil-paper insulating systems, including their thermal, mechanical, and insulating properties, and good results have been achieved.

In 2010, Christopher, A et al. [113] performed electrostatic field simulations to study the effect of barium strontium titanate nanoparticle suspensions on the electric fields within synthetic insulating oil. The simulations confirmed that, by adding high dielectric constant nanoparticles, the electric field of insulating oil can be changed dramatically through charge polarization. The nanoparticles are able to generate large electron extraction fields on the cathode surface and form paths of higher electric field across the gap, which may help to minimize streamer propagation jitter.

Dai et al. [115] studied the dispersion stability of nanoparticles in mineral insulating oil through MD simulation. Their results showed that nano-Al₂O₃ with a diameter of 18 nm forms a stable dispersion in mineral insulating oil. In 2015, Shi et al. [116] studied the effect of nanoparticles on the properties of mineral oil-paper composite insulation systems by conducting experiments and simulation studies. They also compared the operating impulse breakdown voltages of the mineral oil-paper composite insulation system with and without nanoparticles. The group developed a model to describe fluid injection in the oil-paper system, and calculated the electric field in the fluid injection channel along the surface, space charge, and distribution of surface charge along the surface of the insulating paper. It was found that the voltage withstand properties of the modified insulation paper were improved by about 10% compared with those of the unmodified insulation paper. The surface charge density decreased from 0.020 to 0.016 C/m² upon nanoparticle modification, and the nanoparticles restricted the development of fluid injection in mineral insulating oil and fluid injection along the surface, as well as improving the insulation properties of the insulating paper. In 2015, Adil et al. [117] investigated the system's rheological properties and diffusion coefficient, and studied the nanocluster's disperse and stability. The calculated viscosity of the CuO-alkane system was 1.613 mPa s at 303 K.

Zhou et al. [118] studied the heat transfer characteristics of nanomodified mineral insulating oil. To do this, they prepared nano-SiO₂-modified transformer oil with different nano-SiO₂ concentrations, and compared their thermal conductivity values. The results showed that the thermal conductivity of modified mineral insulating oil will gradually increase with rising nano-SiO₂ concentration. Computational models of different kinds of nanoclusters (nano-SiO₂, nano-Al₂O₃, and nano-ZnO) in

mineral insulating oil fluidic systems have been constructed at the atomic molecular level to investigate the effect of temperature on the system viscosity [119]. Simulation results showed that the viscosities of the pure mineral insulating oil and nanofluids decrease as the increase of temperature, and the relationship of viscosity with temperature does not change after adding nanoparticles. The viscosities of nanofluids are higher than that of pure oil, and nano-SiO₂ is the most suitable nanoparticle additive to minimize the increase of viscosity. The viscosity of both pure and nanomodified mineral insulating oil decreases with increasing temperature [120]. The molecular structure of nano-ZnO is shown in Figure 14.

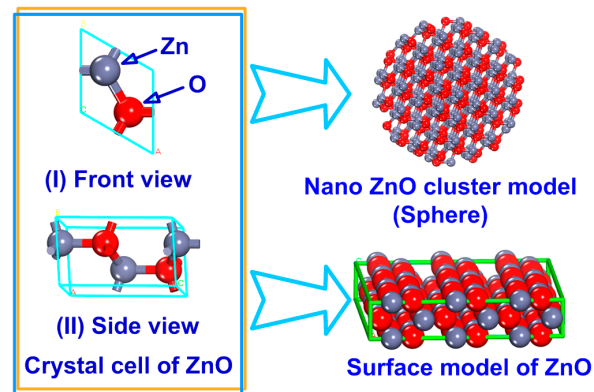


Figure 14. Molecular structure of nano-ZnO.

Moreover, the structural and dynamical properties at the water/oil interface in various systems have been investigated by the dissipative particle dynamics simulations [121]. For all nanoparticles used in literature, as expected, a transition from the liquid-like state to the solid-like state with the surface density increases was observed. However, at the water/oil interface, different nanoparticles have different contact angles, which made the results for systems containing mixtures of nanoparticles more complex.

Shi et al. [122] performed MD simulations to study the microscopic behaviors of anionic, nonionic, and zwitterion at an oil/water interface. Their results showed that these four kinds of surfactants can form a stable monolayer at an oil/water interface. Possover et al. [123] pointed out that because nanofluids have excellent thermal performance owing to their high thermal conductivity, they may show promise as nanofluid coolants that are electrically insulating. By using equilibrium MD simulations followed by the application of the Green-Kubo autocorrelation function, they investigated the thermal conductivity of a BN suspension.

Riku et al. [124] performed a number of MD simulations on nonionic nanoparticle/surfactant systems. Analysis of the results allowed the dispersive interactions of the nanoparticles and surfactants to be related to their physical behaviors at the oil/water interfaces.

Our team studied the effect of nano-SiO₂ on water diffusion and its mechanism in naphthenic-based mineral insulating oil using the MD method. We established a model of mineral insulating oil modified with nano-SiO₂ and different moisture contents (denoted as the modified model in Figure 15a and a model of mineral oil without nano-SiO₂ (denoted as the unmodified model, as shown in Figure 15b, and performed MD simulations to calculate the microparameters of all the models after full relaxation. Figure 15c,d present the statistical results for the Connolly surfaces of the modified and unmodified models, respectively. Preliminary findings indicate that in the case of normal operation of a transformer, addition of nano-SiO₂ will slow the diffusion of water molecules in mineral insulating oil through the adsorption of water molecules in mineral oil, therefore decreasing the probability that water molecules form a small bridge. This simulation revealed why

the breakdown voltage of the mineral insulating oil is improved through the addition of nano-SiO₂ in macroscopic experiments.

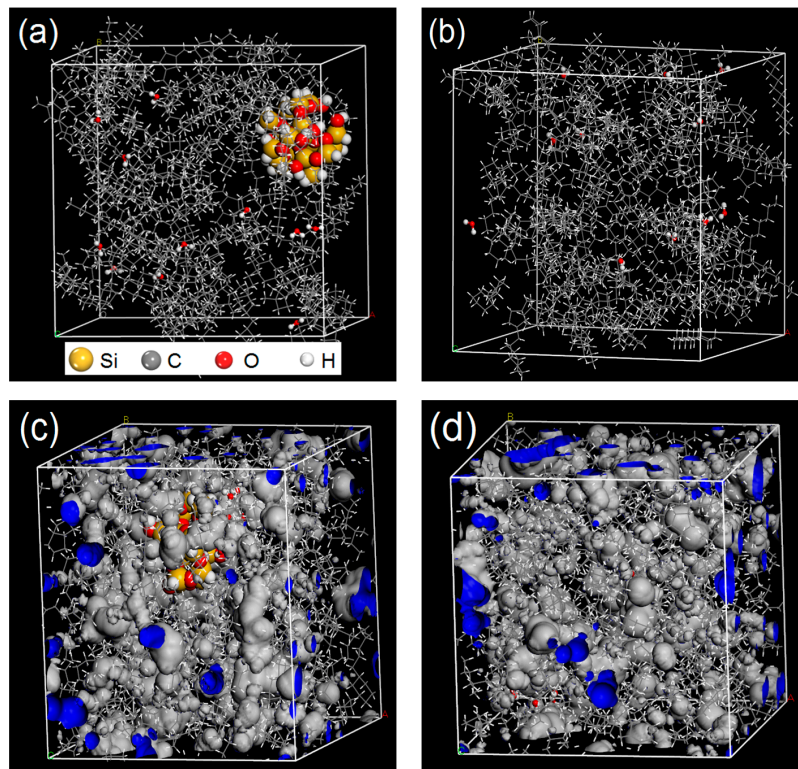


Figure 15. Effect of water on the properties of mineral insulating oil: (a) Modified model; (b) Unmodified model; (c) Statistical results for the Connolly surface of the model in (a); (d) Statistical results for the Connolly surface of the model in (b).

The above examples illustrate that molecular simulation technology plays an important role in the research of mineral insulating oil for transformers. On one hand, molecular simulation technology can explain the appearance of macroscale phenomena, such as the influence of nanoparticles on the viscosity of mineral insulating oil and the temperature dependence of water diffusion in mineral insulating oil. On the other hand, molecular simulation technology provides powerful guidance on how to further improve the performance of mineral insulating oil, such as the type of nanoparticle added, determination of the amount added, and the components in the mixture.

5. Conclusions and Prospects

As research methods for traditional mineral oils have gradually matured, the composition, partial aging, and cracking mechanism of mineral insulating oil were initially learned, and some factors that affect its performance were then studied. On this basis, ways to improve the performance of mineral insulating oil have been proposed. Even so, there are still many problems that are worth exploring, which are summarized as follows:

- (1) With the rise of the operating voltage of power grids, the requirements for the insulation, mechanical, and heat resistance properties of transformers are also gradually increasing. Therefore, it has become important to develop mineral oils with better performance.
- (2) Because mineral insulating oil is a non-renewable resource, it will face shortage and exhaustion issues. At the same time, in the face of growing environmental problems, the use of mineral insulating oil will be further restricted because of its poor biodegradability and environmental risk. Recent studies have shown that vegetable oils are completely biodegradable and

pollution-free [125,126]. Treated plant insulating oil, such as sunflower oil, olive oil, and rapeseed oil, has the advantages of high flash point and large dielectric permittivity, so it is a good substitute for mineral insulating oil [127–129]. However, most vegetable oils possess high viscosity, pour point, and acid content after aging compared with those of mineral oil. Thus, electrical and mechanical equipment will be affected to a certain extent during long-term operation in vegetable oil at high temperature and high pressure [130–132].

- (3) The micromechanics of the discharge process of nanomodified mineral insulating oil is worth studying. For example, the creeping process along the surface of paperboard immersed in mineral insulating oil should be analyzed to reveal the effect of nanoparticles on the microstructure of the mineral insulating oil-paper interface and explore the effect of nanoparticles on streamer development at the mineral insulating oil-paper interface.
- (4) The macroscopic adaptability of nanomodified mineral insulating oil needs to be investigated further. The addition of different nanoparticles influences the improvement of the thermal conductivity of the mineral insulating oil and its overall heat transfer efficiency. Because the mineral oil is used as an insulating medium for the long-term operation of transformers, its insulating, electrical, anti-aging, moisture, and stability (degree of nanoparticle agglomeration) characteristics are all important factors that influence its performance and application.
- (5) The mechanism of nanomodified mineral insulating oil and insulating paper during operation needs to be studied further. The internal insulation of a transformer is mainly a hybrid insulation system consisting of insulating paper and mineral insulating oil. However, there has been no in-depth research on the influence laws and mechanism of nanoparticles on oil-paper hybrid insulation systems. In addition, little research has been reported on the electrical properties and stability of nanomodified oil-paper systems under the conditions of long-term electric/thermal aging and high moisture content. The dielectric constant of oil-paper systems is changed by the addition of nanoparticles, which greatly influences the distribution of electric field in the transformer. However, the mechanism of this effect is currently unclear, so there is a need to focus on the effect of nanoparticles on oil-paper hybrid insulation systems in future research.
- (6) Multidisciplinary integration is a current trend to develop basic theory in mineral insulating oil research. At the macroeconomic level, research on mineral insulating oil involves the basic subjects of classical physics, such as classical mechanics, photonics, and electromagnetism, and at the micro level, the research involves molecular chemistry, surface science, quantum mechanics, and the theory of relativity. The macroscopic behavior and microscopic mechanism of mineral insulating oil must be integrated to fully understand its characteristics.
- (7) Molecular simulation technology will still play an important role in investigating the aging, cracking, and other microscale behaviors of mineral insulating oil. The properties of mineral insulating oil are affected by the complex internal environment of the transformer. Current molecular simulations still require the transformer to have a specific state, so the operating environment of the transformer cannot be completely simulated. Therefore, molecular simulation technology needs to be further developed to better reflect the real operation environment of mineral insulating oil in combination with multifactorial simulation. With the further development of computer technology, especially advances in high-performance calculation, it should be possible to build bigger and more optimized models. Faster operation has also become a trend in the development of molecular simulation technology.

Acknowledgments: The authors wish to thank the guest editor Issouf Fofana for the kind invitation to present this review article in the Special Issue “Engineering Dielectric Liquid Applications”. Besides, the authors wish to thank the National Key R&D Program of China (Grant No. 2017YFB0902700, 2017YBF0902702) for their financial support.

Author Contributions: All authors collected, organized and analyzed the references; Xiaobo Wang and Chao Tang wrote the paper, while other authors offered their modification suggestions for the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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