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Abbreviations and Symbols

PD	Partial discharge
IEEE	Institute of Electrical and Electronics Engineers
ASTM	American Society for Testing and Materials
TAN	Total Acid Number
IFT	Interfacial tension
NTU	Nephelometric Turbidity Units
DDP	Dissolved Decay Product
PDIV	Partial discharge inception voltage
Al_2O_3	Aluminum Oxide
TiO_2	Titanium Oxide
SiO_2	Silicon dioxide
ZnO	Zinc Oxide
UQAC	Université du Québec à Chicoutimi
Cigele	Chaire industrielle sur le givrage atmosphérique des équipements des réseaux électriques

Chapter 1

General Introduction

Chapter 1

General Introduction

1.1 Background

The role of electrical insulation is important, for it provides a foundation for the proper operation of power equipment. Indeed, any electrical equipment consists of a judicious arrangement of conductive materials used to transport electrical energy and insulating materials in order to prevent short-circuits between conductors. The main function of insulating liquids is to transfer heat away from power equipment, such as transformer core and windings and to act as an electrically insulating medium. In almost 90% of power transformers, mineral oil is used as an insulating material. Mineral oil is a by-product of the refining of crude petroleum and is a mixture of many different hydrocarbon compounds.

Under service conditions, the insulation is often subjected to gradual deterioration due to electrical, thermal, mechanical, and chemical stresses. Moreover, the interaction among these stresses can cause premature aging of the insulation or, in extreme cases, failure. This reduces the efficiency of the oil as a heat transfer medium and as a dielectric material [1-3].

This master's thesis aims at investigating the effect of chemical impurities (aging by-products) on partial discharge inception voltage (PDIV) as a basis for condition assessment. Needle-plane electrode geometry will be employed, since this configuration is necessary for any practical diagnostic based on partial discharge (PD). Such fundamental studies on the pre-breakdown phenomena in insulating liquids are still poorly understood despite the extensive work carried out [4, 5].

The widespread use of transformer oil for high voltage insulation and cooling of power equipment has led to extensive research investigations aimed at enhancing both its dielectric and thermal characteristics. A particularly innovative example of such work is the development of dielectric nanofluids [6, 7]. These materials are manufactured by

adding nanoparticle suspensions to transformer oil, with the aim of enhancing its insulating characteristics [8-11].

Nanofluids, a relatively new class of fluids, consist of a base fluid with suspended nano-sized particles (1-100 nm). These particles, generally a metal or metal oxide, increase the conduction and convection coefficients, which consequently enhance the heat transfer rate out of the coolant [8].

1.2 Research Problem

Dielectric liquids have a wide range of applications for cooling high voltage insulation and power equipment, because of their greater electrical breakdown strength and thermal conductivity compared to gaseous insulation. However, failure in liquid insulation can cause major damage to the power equipment and surrounding area sometimes leading to injuries and fatalities. As well, liquid insulation failure frequently leads to major operational disruption, financial losses, and possible environmental legal action against owners of the failed equipment. In addition, liquid insulated high voltage equipment, such as power transformers, are extremely expensive and play an important role in electrical transmission and distribution systems. Consequently, utilities and power system operators frequently monitor the insulation system for operational safety.

Understanding the fundamental theoretical causes of oil breakdown, that is, the conditions necessary for electron avalanche formation, is important to properly design power equipment. Accordingly, a thorough understanding of the physical mechanism by which partial discharges are initiated remains a vital investigative goal. Every discharge event causes a deterioration of the material because of the energy impact of high-energy electrons or accelerated ions. Exposure of organic insulating materials to PD causes physical erosion due to impact of charged particles on the cavity walls. This is accompanied by chemical deterioration as the hydrocarbon molecules undergo bond scission. Various gases are formed inside the cavity as a result of the reactions that occur with oxygen. Gas pressure changes within the altered atmosphere of the cavity; together

with the change of the wall surface conductivity, the discharge behavior within the cavity is modified. PD gives rise to physical and chemical degradation of the insulation system [5, 12].

Protracted partial discharge can erode/degrade insulation and eventually lead to its breakdown and subsequent destruction of the power transformer. Unexpected failures cause major disturbances to operating systems, resulting in unscheduled outages and power delivery problems. Extreme reliability is demanded of electric power distribution systems because any failure inevitably leads to high repair costs, long downtime and possible safety risks to personnel. In addition, environmental aspects, such as consequential damage, fire and pollution are of high risk. Transformer failures can cost up to $15 million, in addition to ruining an operator's reputation. These enormous costs provide ample incentive for electric companies to ensure reliability and availability throughout the life cycle of its important assets.

Because of the potentially disastrous outcomes of insulation failure, researchers have studied the insulating properties of dielectric liquids to understand the fundamental mechanisms that can cause electrical breakdown. Furthermore, many alternatives have been proposed to enhance insulation properties [5-16]. Among these, the use of nanoparticles has been proposed [9, 11, 13]. Although the AC (60 Hz) dielectric strength of nanofluid can be increased, any increase in the loss factor may cause thermal problems in real applications. Any prospect of a new type of nanoparticle-based nanofluids needs to be explored in order to improve the insulating and anti-aging properties of mineral oil, while keeping other basic electrical parameters almost constant.

1.3 Objectives

This research project involves fundamental studies on the conduction and breakdown phenomena in insulating liquids. The objective of this project is primarily to

understand the influence of the fluid properties on the pre-breakdown phenomena that are still poorly understood despite extensive work carried out in recent years.

Fundamental studies using modern equipment, involving physico-chemical testing (turbidity, acidity, IFT, etc.) and enabling some correlations with partial discharges will be addressed. These investigations should aid in finding relationships between the PDIV and the other physico-chemical parameters of oil.

Another important objective of the proposed research is to improve the present dielectric properties of insulating oils through the incorporation of nanoparticles in order to provide the required characteristics of new insulating fluids to meet current and future requirements of the power industry and utilities.

1.4 Methodology

Aging is a gradual change of oil state and its properties that usually leads to a degree of breakdown. Aging is an irreversible deleterious change to the serviceability of an insulation system. Aging is simulated in the laboratory by placing oil samples in a convection oven at 100 $^\circ$C for specific durations, under air inlet. For different aging duration several parameters will be assessed. The investigations will also be performed on new oil to provide baseline comparison.

In the second part of this research project, the electrical properties of the mineral oil with addition of different amounts of TiO_2 nanoparticles were investigated at temperatures ranging from -47°C to +47°C.

Transformer oil properties can be classified into three categories, namely, physical, electrical, and chemical properties. The following standards were used to assess oil properties during this research project.

1.4.1 Physical properties

1.4.1.1 Water Content (ASTM D 1533)

By using the Coulometric Karl Fisher titration apparatus (Figure 1.1), the quantity of water content in the oil was determined. The test was repeated three times for each series of tests, and a mean value considered for each analysis [14]. The results are provided in ppm. Oil quantity needed for this test was 3 x 1 ml with ideal value(s) being below 5 (ppm). The water content must be low. Indeed, water content is enemy number one of electrical power equipment because it increases electric conductivity and dissipation factor and can harmfully affect the dielectric strength of insulating oils [15].
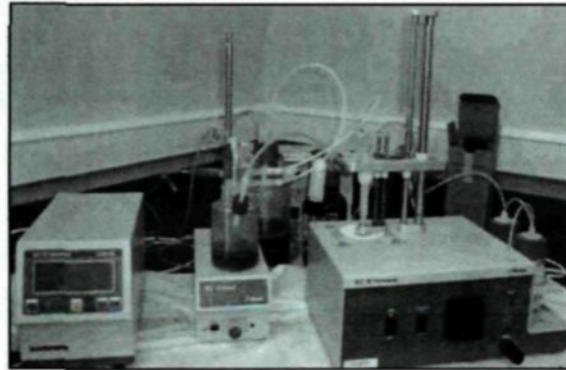
Figure 1.1. Karl Fischer (Model KF 831).

1.4.1.2 Interfacial Tension (ASTM D 971)

Using this test (Figure 1.2), it is possible to determine the oil's soluble polar contaminants, which reduce the molecular attraction force between the oil and the water. The measuring unit is dynes/cm. The oil quantity needed for this test is 50 ml [16].

The Interfacial Tension against water (or IFT of oil) is the force in dynes per centimetre required to rupture the oil film existing at an oil-water interface. When certain contaminants, such as soaps, paints, varnishes, and oxidation products, are present in the oil, the film strength of the oil is weakened and is thus more easily ruptured. For oils in service, a decreasing value indicates the accumulation of contaminants, oxidation products, or both. It is a precursor of objectionable oxidation products that may attack the insulation and interfere with the cooling of transformer winding [15].

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Figure 1.2. Tensiometer for measuring the interfacial tension of a liquid.

1.4.2 Electrical properties

1.4.2.1 The dielectric constant (ASTM D 924)

Insulating liquids are generally used either to insulate components of an electrical network from each other and from ground (alone or in combination with solid insulating materials) or to function as the dielectric of a capacitor [17]. The dielectric constant (or relative permittivity) of a material under given conditions shows the level at which it concentrates electrostatic lines of flux. In technical terms, it is the ratio of the amount of electrical energy stored in a material by an applied voltage, relative to that stored in a ·vacuum.

The Novocontrol Beta advanced impedance analyser (Figure 1.3) is an instrument used to measure the dielectric characteristics from a frequency range between 3 µHz and 20 MHz [18].

Figure 1.3. Novocontrol Beta advanced impedance analyser.

1.4.2.2 Dielectric breakdown voltage (IEC 60156)

The dielectric breakdown voltage of an insulating liquid is the measure of the liquid's ability to withstand voltage stress [19]. Low values of breakdown voltage indicate the presence of moisture and conducting substances within the oil [15].

Figure 1.4. Liquid dielectric test set.

Partial Discharge Detector (DDX 7000)

The DDX 7000 (Figure 1.5) is used to detect and measure partial discharge activity in high voltage insulation. The level of partial discharge is expressed in pico-coulombs

(pC). Any power equipment that contains electrical insulation materials presents some degree of partial discharge. Acceptable partial discharge levels will be different depending on the application, the customer, and the reliability level needed. Below is a partial list of some finished goods that are commonly tested for partial discharge and what some common typical levels are:

- Power Cable < 2 pC,
- Switchgear < 100 pC,
- Power Transformers <500 pC,
- Bushings < 20pC [20].

The oil quantity needed for this test is 1000 ml. The PDIV will be the level of voltage corresponding to 100 pC [20].

Figure 1.5. Partial Discharge Detector (DDX 7000).

1.4.2.3 Resistivity (ASTM D 257)

Resistivity is the resistance to leakage current through an insulating material. The lower the volume resistivity, the higher the leakage current and the more conductive the material is. Good transformer oil resistivity should be high. Lower transformer oil resistivity indicates the presence of moisture and conductive contaminating agents. High resistivity reveals fewer free ions and ion-forming particles and normally indicates a low concentration of conductive contaminants.

Since insulation is meant to have large resistivity, measuring that resistivity is difficult; therefore appropriate equipment and test method should be used. Electrometers

(Figure 1.6) are capable of measuring low current [21]. ASTM D-257 [22] is the test method used for measuring the resistivity of insulating materials.

Figure 1.6. Model 6517A electrometer/high resistance meter.

1.4.3 Chemical properties

1.4.3.1 Acidity or TAN (ASTM D 664)

This test method (Figure 1.7) is employed to determine the approximate total acidic constituents or contaminants in the electrical insulating liquid. The results are reported in mg of KOH/g for each sample [22]. Oxidation of the transformer oil occurs due to reactions involving the hydrocarbon molecules of oil and oxygen. Copper, presents in the transformer, acts as catalyst in this reaction. The increase in oil acidity is an indication of aging though service. Acidic by-products have an impact on the degradation of cellulosic materials and may contribute to the corrosion of a transformer's metal parts [15]. Thus the measurement of the total acidity is a way to determine the oil quality during the life of the transformer.

Figure 1.7. Experimental setup for measuring the acidity of liquid.

1.4.3.2 Turbidity (ASTM D 6181)

This test method is a laboratory procedure that ascertains the quantity of suspensions in insulating oils of petroleum origin using a nephelometric measurement technique (Figure 1.8) to determine fluid turbidity. This test method is designed to reveal changes that may occur in the oils. The results will be recorded in NTU (Nephelometric Turbidity Units) [26].

Figure 1.8. Turbidity meter for measuring cloudiness of liquid.

1.4.3.3 Dissolved Decay Product (ASTM D 6802)

This test method uses a spectrophotometer (Figure 1.9) to characterize the relative level of dissolved decay products in mineral insulating oils of petroleum origin. While new oil is almost transparent to a monochromatic beam of light in the visible spectrum,

the increasing concentration of dissolved decay products shifts the absorbance curve to longer wavelengths [27].

Figure 1.9. Spectrophotometer for measuring the relative amount of dissolved decay products.

1.5 Statement of the originality of the thesis

The extensive use of transformer oil for high voltage insulation and power apparatus has led to extensive research investigations, but very little information is available about how PD sequence formation is influenced by the chemistry of the insulating liquid and its impurities. It remains undetermined if some relationship exists between PDIV characteristics and the degree of aging.

One of the important factors to enhance the life of transformer and service security of power transformers is to diagnosis the power transformer. One of the most important key to diagnosing the power transformer is to identify the partial discharge (PD). Furthermore practical methods to estimate the remaining lifetime of the oil specimens include measuring acidity, turbidity, water content, IFT and DDP of transformer oil. Correlation between PDIV and measured acidity, turbidity, water content, IFT and DDP of transformer oil is investigated in this research project.

Another important factor that can increase the life of transformers is to improve the dielectric properties of the insulating oil. The first attempt to increase life of transformer is to add nanoparticles to transformer oil and thereby increase the dielectric properties of transformer oil in terms of improved electrical insulation performance, safety, reliability and efficiency, during cold winter days in nordic regions.

1.6 Overview of the thesis

This Master thesis is subdivided into five chapters. After a general introduction in Chapter 1, a review of the behavior of insulating oils under high fields as well as a partial discharge study are presented in Chapter 2. Chapter 3 emphasizes the role of the aging process in mineral oil on partial discharge and some of the oil's physico-chemical properties. Some correlations between PDIV and the other parameters of oil are also addressed. In Chapter 4, dielectric characteristics of oil are introduced and aimed at enhancing the insulating properties of mineral oil by the addition of nanoparticles.

Finally, some general conclusions are summarized in Chapter 6, from analyses and discussions of the results reported in the previous chapters. In addition, some recommendations are provided for future research.

Chapter 2

Literature review

Chapter 2

Literature review

2.1 Introduction

Partial discharge (PD) is a localized electric breakdown of a small portion of an insulation material under high voltage stress. This phenomenon occurs when the applied voltage exceeds the partial discharge inception voltage (PDIV), which only partially bridges the insulation between conductors. Partial discharge occurrence in dielectric liquids unambiguously implies the existence of gaseous cavities within the liquids.

Insulating materials sometimes contain voids or cavities; PD usually begins within voids or in bubbles within liquid dielectrics. The dielectric constant of the void is less than the surrounding dielectric, so that the electric field strength in the voids is higher than that across the dielectric. Thus, even under normal operating voltage, the voltage stress in the voids may increase over their PD inception voltage (PDIV) so that PD activity will start within the void.

Different partial discharge detection and measurement procedures suitable for use on cables, capacitors, transformers and rotating machines have been examined and compared [23].

The state-of-the-art research on partial discharge is discussed in section 2.2, followed by the concept of enhancing mineral oil's breakdown voltage by adding nanoparticles to it in section 2.3.

2.2 Partial discharge

Pioneering works by Mallet can be considered as the first attempt to describe the behavior of insulating liquids under high fields [24]. Thus far, various methods have been developed for studying pre-breakdown phenomena and partial discharges. The step

method used here is an improvement of a method developed by a CIGRE Task Force TF 15-02-02 [24], which involves measuring the partial discharge inception voltage (PDIV) in a highly non-homogeneous field (needle to sphere gap). Preliminary tests showed that the CIGRE method does not characterize the volume of the liquid. This defect is overcome by the proposed step method. Results on the effects of conditioning and aging obtained with the proposed technique are presented in [24].

In the last two decades, many studies of the partial discharge phenomenon in solid dielectric systems have been published. However, only a few limited reports have been included in the literature on partial discharges in liquid dielectrics. In 1992, C. Mazzetti and M. Pompili [25] did an investigation to study the partial discharge behavior of some well-defined dielectric fluids such as phenyl xylene ethane, ditolyl ether, mono and dibenzyl toluene and perfluoro polyether. The partial discharge inception and extinction voltages of these fluids were determined under uniform and non-uniform field conditions [25].

Also in 1992, Bezborodko, Lesaint and R. Tobazéon investigated the gassing phenomena under an AC voltage in various dielectric liquids that were subjected to partial discharges produced in different gases [26]. The roles of the numerous experimental parameters that affect the results have been extensively studied using a uniform field test cell. First of all, they show that given the classical PD equivalent circuit, a more refined analysis permits a good description of the influence of parameters upon gas volume variations and discharge characteristics. Such parameters include gas and solid thickness as well as the amplitude and frequency of the applied voltage. These results allowed for obtaining suitable measurements of the charge and energies involved in the gaseous discharges, from which the energy required to absorb (or to create) a gas molecule were deduced. This gassing energy, which is independent of the experimental parameters, is characteristic of each gas/liquid pair and constitutes a valuable quantitative evaluation of gassing properties [26].

In 1993, Hisanao Yamashita published a paper in which current pulses caused by partial discharges (PD) were measured using LEDs and fiber optics under impulse voltage conditions [27]. This system has the advantage of having good isolation from the HV power supply and no effect from electromagnetic noise compared with usual

systems. This system can detect a PD pulse having a half width of 3 ns; it also has the capability of measuring PD pulse charges in the range of 1 to 2000 pC, when the optimum dc bias is applied. Finally, PD pulses and light emission or streamer formation in dielectric liquids were measured simultaneously by using an image converter camera [27].

Several scientists explain the initiation of PD in insulating liquids by assuming the breakdown of gas-filled voids [4, 5]. Others attribute the initiation more generally to impurities, suggesting that space charge effects are necessary for the generation of PD. In 1994, Borsi et al. investigated the effect of temperature, water content, pressure and oil condition on the PDIV [28]. They investigated the shape of the PD pulse and the behavior of visible channels by using schlieren techniques [28]. In 1999, they also showed the influence of different parameters, such as needle-tip radius and gap distance on PDIV and other PD characteristics. They compared their results to the theoretical macroscopic field

(E_p) at the needle tip: $E_p = \dfrac{2U(t)}{r \ln 4(\dfrac{d}{r-1})}$.

where r is the needle-tip radius, d is the gap length and U(t) is the applied voltage [29].

In 2003, H. Shiota studied PD phenomena by measuring the PD characteristics and by observing the behavior of bubbles in oil. The experimental results showed that the PD strongly depended on the size of bubbles [30]. PD measurements in dielectric liquids have been performed in the past by using only conventional narrow bandwidth detectors. The more recent use of ultra-wide bandwidth instruments has once again bolstered the thesis that PDs in oils are the consequence of the streamer (vapor phase) formation and its development. Partial discharge measurements are an important diagnostic tool to monitor the condition of a transformer's insulation.

In 2005, Regier performed simultaneous measurements using 1) a detection circuit based on the IEC 60270 recommendations and 2) a wide-band UHF system. With the IEC 60270 based measuring system, the PD magnitude and phase-resolved PD patterns can be acquired. The UHF system measurements are performed in both frequency and time domains. By using the spectrum analyzer as a band pass filter, a phase resolved PD pattern can be obtained as well [31].

In 2008, Pompili presented simultaneous PD measurements in insulating liquids using both narrow and ultra-wide bandwidth [32]. Whilst PD detection with narrow bandwidth instruments gives only integrated signals, the use of ultra-wide bandwidth techniques provides more precise information on PD phenomena, which appear to be in the form of pulses. The use of the ultra-wide bandwidth instruments also allow us to distinguish the PD pulses occurring in regular voids of oil-paper insulations and PD pulses formed directly in the liquids due to the streamer development [32].

In 2008, Pompili, Mazzetti and Bartnikas suggested a test procedure for measuring the partial discharge inception voltage (PDIV) in dielectric liquids [33]. In this method, the antecedent IEC point-to-sphere test cell arrangement is replaced by a point-to-plane one. A dual ultra wide-narrow bandwidth PD detection system is employed, which enables distinguishing the PD pulse-burst discharges that occur in liquid dielectrics from the normal PD discharges that characterize stable voids occluded within solid-liquid insulation systems [33].

Most of the authors who worked on corona discharge in oil did not consider the needle length. Brammer et al, in [34] discussed the geometry dependence of the electrical field around the needle tip. In 2010, M. Ghafarraian showed that corona inception voltage is dependent on the electrical field around the needle tip. Also, the corona inception voltage is dependent on needle length and distance between needle tips and ground electrode [35]. He also showed that when the oil temperature is increased, the inception voltage also increased; in contrast, the corona repetition rate is decreased [35].

When water content in oil reaches the saturation point, it is separated out to form free water, resulting in a two-phase system. Free water is considered the number one contaminant in oil. The relationship between water solubility and temperature is almost always exponential. Indeed, $W_L = K.e^{-H/T}$ where H and K depend on the liquid itself and have to be determined experimentally.

Figure 2.1 shows the solubility of different fluids in water as a function of temperature. The y-axis is logarithmic and W_0 and H are always constant for each fluid as it depends on characteristics of each fluid. Hence, the higher the temperature, the greater water content is in the oil [36].
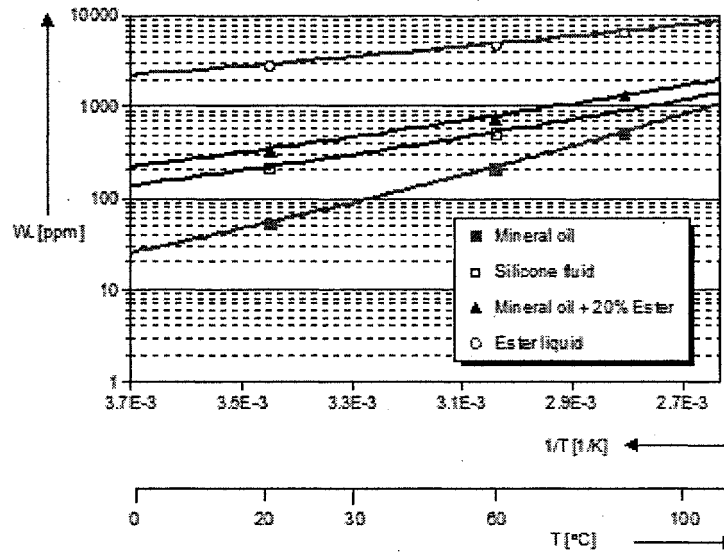
Figure 2.1. Solubility of water in oil as a function of temperature [36].

The relative humidity Wrel(%) at the given temperature T(K) is the ratio of the absolute water content in liquid W_{abs}(ppm) to the saturation limit W_L(T). Figure 2.2 shows breakdown voltage of different fluids as a function of Wrel(%) [36]. As shown in this figure, with a decrease in Wrel(%), the breakdown voltage increase. This is explained as follows. Considering a plane-to-plane electrode filling with oil and W_{abs}=20 (ppm); with an increase in temperature, W_L(T) will also increase. With an increase in W_L(T), the Wrel(%) will decrease and the water molecules inside oil will decrease. Water molecules are conductive, so any increase of water content hastens breakdown. Thus, breakdown voltage is increased whenever water content is reduced.

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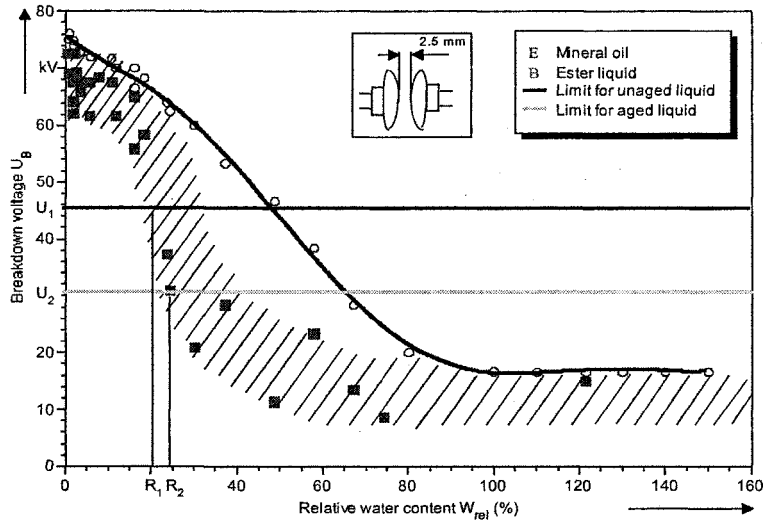
Figure 2.2. Breakdown voltage of different fluids as a function of Wrel(%) [36].

2.3 Nanofluids

The laboratory that pioneered the idea of nanofluids was The Argonne National Laboratory (Illinois, U.S.A), which applied nanotechnology to thermal engineering [37]. Choi (1995) coined the term nanofluids (nanoparticle fluid suspensions) to describe this new class of nanotechnology-based heat transfer fluids. Since Choi brought forward the novel concept of nanofluids in spring 1993, talented and studious thermal scientists and engineers in the rapidly growing nanofluids community have not only discovered the thermal properties of nanofluids, but are also developing other characteristics of nanofluids. As a result, the research topic of nanofluids has been receiving increased attention worldwide [7].

The most commonly used methods for producing nanofluids are discussed in section 2.3.1 followed by applications of nanofluids and their characterization in sections 2.3.2 and 2.3.3, respectively. Then, in section 2.3.4, the previous research using nanofluids to enhance dielectric characteristics are investigated.

2.3.1 Techniques used in the synthesis of nanofluids

2.3.1.1 Two-step technique

In this technique, dry nanoparticles are first produced as a dry powder and then dispersed into a proper fluid. The disadvantage of this method is the unavoidable clustering and aggregation of the nanoparticles because of their high surface energy. Therefore, the particles tend to form sediment and clog at the bottom of the container. Some authors [6, 7] consider that this method is successful for oxide nanoparticles in de-ionized water because such particles are easy to make and are chemically stable in solution. The main advantage of this method is its low cost and commercial availability. Due to its simplicity of preparation, this technique is attractive for the industry [6, 7, 37, 38].

2.3.1.2 Single-step technique

With this "single-step" technique, the nanoparticles are simultaneously made and dispersed directly into the liquid. Figure 2.3 shows the diagram of a one-step production system, the 'direct-evaporation' technique which was developed by Choi et al. [6, 7]. The main problems with this technique are related to both the necessity of using low vapor pressure liquids and its limited production. However, this method avoids drying, storage, transportation, and dispersion of nanoparticles.
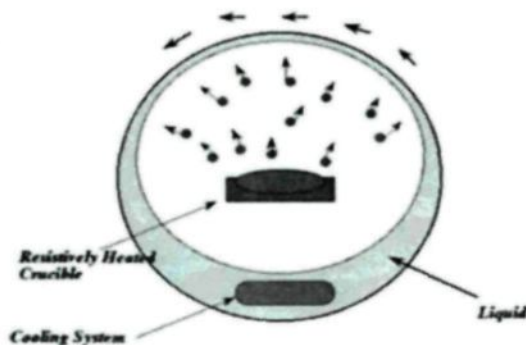
Figure 2.3. The 'direct-evaporation' technique, developed by Choi *et al.* [37].

2.3.2 Applications of nanofluids

1) Heat transfer intensification: Examples of such applications are in electronics, industrial cooling, building heating, pollution reduction, nuclear systems cooling and space and defense.

2) Mass transfer enhancement

3) Energy applications: Such applications are energy storage and solar absorption.

4) Mechanical applications: Such applications are friction reduction and magnetic sealing.

5) Biomedical applications: Such applications are antibacterial activity and nondrug delivery.

6) Other applications: For example, micro-reactor intensification, nanofluid-based microbial fuel cells, nanofluids as vehicular brake fluids, nanofluids with unique optical properties. [8, 38].

2.3.3 Characterization of nanofluids

2.3.3.1 Preparation

It is essential to obtain a homogeneous suspension without any aggregation and clustering during nanoparticle formation. A. Ghadimi et al. have shown the following helpful methods to prevent sedimentation of nanofluids: ultrasonic vibration, pH control (surface chemical adding) and addition of a surfactant or activator [6].

1) Ultrasonic vibration: This method is a powerful tool for breaking down the agglomerations when compared to others like magnetic and high shear stirrer that have been used [6].

2) pH control (surface chemical adding): The electrokinetics properties of aqueous nanofluids are directly linked to their stability. Xie et al. [6] showed that by simple acid treatment a carbon nanotube suspension gained good stability in water.

3) Addition of surfactant or activator: Surfactants are used to prevent particle agglomeration during nanoparticle formation and to ensure the formation of miniscule nanoparticles.

2.3.3.2 Stability of nanoparticles

There are several ways to investigate the stability of nanoparticles. Those most commonly used are optical spectroscopy, transmission electron microscopy, x-ray diffraction, infrared, Raman and other types of spectroscopy, and Zeta potential [6, 7].

1) Optical spectroscopy: This method is good for metal nanoparticles, particularly gold. When an electromagnetic wave passes through a fluid, the absorption and scattering of light is different. At 200-900 nm wavelengths, it measures the absorption of the liquid and is able to analyze the particle size by the peak value as the concentration of the suspension has a linear relation absorbance.

2) Transmission electron microscopy: Two useful data can be obtained through this method: particle size distribution in terms of diameter and standard deviation and the crystallinity of a sample. Information available about nanoparticles are: shape, size, and dimension.

3) X-ray diffraction: This is an important method expanding the understanding about certain properties of synthesized materials.

4) Infrared, Raman and other types of spectroscopy: Spectroscopy is an ideal tool to understand molecular vibrations in nanomaterials. For metal nanoparticles, Raman spectroscopy is used. X-ray spectroscopy is ideal for gold nanoparticles,

5) Zeta potential measurement: This is a critical test to validate the quality of the nanofluids stability via a study of its electrophoretic behavior. According to the stabilization theory, the electrostatic repulsions between the particles increase if zeta potential has a high absolute value which then leads to a good stability of the suspensions [6].

2.3.4 Enhancing oil dielectric characteristics by adding nanoparticles

In 2008, Hwang *et al.* [39] through the use of numerical simulation showed that transformer oil-based nanofluids with conductive nanoparticle suspensions have higher voltage breakdown than pure transformer oil. This behavior is due to the trapping of fast electrons onto slow-conducting nanoparticles, resulting in slower positive streamer velocities and higher breakdown voltage.

In 2010, Yue-Fan *et al.* [9, 40] developed a new type of transformer oil by boosting mineral transformer oil with TiO_2 nanoparticles to enhance its dielectric performance. They showed that TiO_2 nanoparticles could enhance the breakdown voltage under AC conditions. The inclusion of such nanoparticles provides scattering obstacles and trap sites in the charge carrier paths, effectively reducing carrier mobility and thereby carrier energy. They also prepared three kinds of TiO_2 nanofluids based on transformer oil [13]. They showed that the breakdown strength of oil with non-treated TiO_2 nanoparticles can be improved, but that breakdown strength will decrease at high particle concentration because of the increasing probability of physical agglomeration between the nanoparticles. In contrast, TiO_2 nanoparticles modified by stearic acid can be used to

improve the breakdown strength of mineral oil. At the other extreme, TiO_2 nanoparticles modified by silicone oil decrease the breakdown strength of the oil sample, so these researchers strongly recommended using care while choosing the type of modifying agent.

In 2010, Yeckel et al. [41] investigated the effect of barium strontium titanate (BST) nanoparticle suspension on electric fields within synthetic oil dielectrics. Their simulation showed that adding nanoparticles with a high dielectric constant to oil can change the electric field through charge polarization. Their simulation also showed that increasing the concentration of nanoparticles leads to increasing capacitance between the electrodes.

In 2010, Zhang et al [42] prepared nanomodified insulating vegetable oil through homogeneous precipitation deposition of ferroferric oxide nanoparticles. It was characterized by laser nanoparticle size analyzer. They showed that the ferroferric oxide nanoparticles with suitable concentration improved the breakdown voltage, volume resistivity, electrical strength of the insulating vegetable oil.

In 2011, Yu-zhen Lv et al [43] prepared three kinds of nanofluids by dispersing Al_2O_3, SiO_2 and TiO_2 nanoparticles in mineral oil to improve its dielectric performance. They observed that adding semiconductive nanoparticles to base oil can improve breakdown strength at the optimum concentration of nanoparticle. Furthermore, it was found that the breakdown strength of a particular nanofluid strongly depends on its dielectric properties. They suggested that TiO_2 is a useful modifier to improve the breakdown strength of mineral oil because of its large dielectric constant.

In 2011, Mergos et al [44, 45] carried out a research on the polarization phenomena by adding fine metal oxide powders and nanopowders of Al_2O_3, TiO_2, CuO, Cu_2O and Fe_2O_3 in paraffin oil at concentrations up to 5% w/v in liquid matrix. The results showed that the highly hygroscopic and reactive Al_2O_3 nanopowder induced dielectric behavior that was annulled by adding TiO_2 nanopowder. TiO_2 nanopowder and Fe_2O_3 fine powder increase the relative permittivity in all frequency ranges. Finally, CuO and Cu_2O fine powder show a different mechanism at the high end of the frequency range.

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In 2011, Jian-Quan *et al.* [46] studied the AC and lightning breakdown voltages of transformer oil and transformer oil fortified with semiconducting nanoparticles. They found that the mean AC breakdown voltage and lightning breakdown voltage of nanofluid with optimum concentration was 1.6 times and 1.24 times that of the base oil, respectively. Their group also [47, 48] compared the breakdown strength and PDIV characteristics of aged transformer oil and aged transformer oil-based TiO_2 nanofluids. The aging condition was 130°C for 6 days. They performed AC breakdown voltage and PDIV tests that applied ASTM standards [47, 48]. They showed that the mean value of PDIV in aged nanofluid increased 1.16 times more than in untreated mineral oil.

In 2011, Liu *et al.* [49] investigated the dielectric frequency response of oil-paper composite insulation modified by TiO_2 nanoparticles to improve insulation characteristics. The results indicated that the presence of nanoparticles improved the oil's withstand field strength and complex permittivity.

In 2012, Du *et al.* [50] used the thermally simulated current method (TSD) and pulse electroacoustic technique (PEA) to measure charge trap and transportation characteristics of pure oil and transformer oil-based TiO_2 nanofluids. The test results showed that shallow trap density and charge dissipation velocity in semiconductive nanofluids (SNF) are increased compare to those in transformer oil. Increasing shallow trap density in SNFs could convert fast electrons to slow electrons by the trapping process and could improve breakdown performance of SNFs. In another study [51], they measured AC, DC and lightning impulse breakdown voltage and partial discharge of oil sample before and after adding TiO_2 nanoparticles. It was shown that SNFs have AC, DC and lightning breakdown voltage up to 1.2 times higher than those with pure oil. The partial discharge resistance of SNFs was also improved.

In 2012, Sikdar *et al.* [52] presented the electrical conductivity of water-based TiO_2 nanofluids. Then, Konakanchi et al. [53] measured the conductivity of three nanofluids which were produced by dispersing Al_2O_3, SiO_2 and ZnO nanoparticles in propylene glycol and water, respectively. Both results indicated that the conductivity of the nanofluid increases with temperature and nanoparticle concentration.

In 2012, Li *et al.* [54] dispersed Fe_3O_4 nanoparticles in vegetable insulating oil to improve the breakdown and dielectric properties of the oil. The results indicated that the breakdown voltage and relative permittivity of oil are improved while volume resistivities and dissipation are approximately equal in both fluids.

In 2012, Mansour *et al.* [11] revealed that adding TiO_2 nanoparticle to transformer oil using cetyltrimenthylammonim bromide (CTAB) as a dispersant increases the breakdown strength of oil. They also found that the amount of dispersant has a great effect on the dispersion of nanoparticles.

In 2013, Hanai *et al* dispersed three kinds of metal oxide nanoparticles- TiO2-anastase, TiO2 rutile, and ZnO- to mineral oil and alkyl benzene and measured the breakdown voltage and relative permittivity. Two results were obtained. First, breakdown voltage increased regardless of the kind of nanoparticle or base oils in the domain of 0.05 vol% or less. However, if the concentration of particles goes above 0.05 vol%, the breakdown voltage decreased. Second, the measurement results of relative permittivity with dispersed TiO_2-anatase and TiO_2-routile nanoparticles in mineral oil were in agreement with the calculation results of the randomly arranged model. However, the measurement results of relative permittivity of mineral oil with dispersed ZnO, and the alkyl benzene with dispersed TiO_2-anastase were different from the calculation results of the randomly arranged model. Possibly, a layer with a high dielectric constant was formed on the nanoparticles surface by a correlation with the oil. [55].

In 2013, Bollinger *et al*, studied partial discharge (PD) characteristics of hexadecane in a needle-plane electrode geometry under AC field. PD experiments were conducted on samples containing known concentrations of oil/paper degradation compounds. Partial discharge inception voltage (PDIV), streamer repetition rates, and phase resolved PD (PRPD) patterns were developed. Ionization potentials (IP) and electron affinities (EA) of hexadecane and a selection of additives were calculated with density functional theory (DFT) and were correlated to PD characteristics. IP did not have a significant effect on the number of streamers initiated since most additives had higher IP relative to hexadecane. The presence of electronegative oxygen changes the PD characteristics substantially and, for most additives, increased the number of positive and

negative streamers initiated. The greatest changes in PD characteristics, i.e. a reduced number of negative streamers, was observed for compounds with large electron capture cross sections, even those with negative EA [56].

Chapter 3

Characterization of partial discharges in transformer oil

Chapter 3:

Characterization of partial discharges in transformer oil

3.1 Introduction

As natural degradation is often slow for testing insulation performance of transformer oil over its whole lifespan, the investigation was based on studying the aging effect with accelerated speed in laboratory conditions. The aging tests performed according to ASTM D 1934 enable studying the stability of electrical insulating oil under oxidative conditions. Transformer oils were oxidized under thermal stress and oxygen inlet, particularly in the presence of moisture and metallic particles [2]. The aging procedure was done at different aging times. For each aging time, water content, acidity, DDP, IFT, turbidity and PDIV are determined. Investigations were also performed on new oil to provide a baseline for comparison.

3.2 Experimental setup

Before starting the tests, the mineral oil was degassed and dehumidified by using a dehydrator (Figure 3.1). The drying and degassing of the liquids took place in a two-stage drying unit developed at UQAC. The preparation guarantees low gas content of less than 0.5% as well as a very low water content of less than 3 ppm. The main components of the system as follows:

1- Storage tank: it is a container used for storing mineral oil before the degassing and dehumidifying procedure.

2- Pump: the aim of this pump is to circulate oil, clockwise, at a specified speed.

3- Fine filter: this consists of sheet of paper having pores of 5-μm radius. The aim of this filter is to remove contaminants from the mineral oil. Ten fine filter papers were used in this system to remove contaminants.

4- Pressure reducer: the drying took place in two-stage packed columns. The insulating liquid sample flows successively through a fine filter (3), a one-way valve pressure reducer (4), a heat exchanger (5) and into the first column stage (6). In this stage, the insulating liquid flows at a pressure of $P1 = 1$ mbar and a temperature of $T1 = 50°C$ through Rasching rings. It is then degassed and dried before arriving into the second stage with $P2 = 0.1$ mbar and $T2 = 60°C$. Here the water and gas contents continue to be reduced. The drying lowers the water content from the grade as delivered, to a few ppm (i.e. <5 ppm for mineral oil) from an initial approximate value of 80-200 ppm for liquid ester and an approximate value of 15-20 ppm for mineral oil.

5- Heat exchanger: it is a device built for transferring heat from one liquid to another without allowing them to mix. A solid separates the fluids and prevents them from mixing. One of the fluids runs through the spiral tube while the other fluid runs over them, causing it to be heated. In the system, the fluid that runs over the spiral tube is hot water while the second fluid in the spiral tube is mineral oil. The tube is spiral-shaped because it allows the oil to remain in the tubes for longer time period.

6- 1st column stage: it is a column with double septa between which there is hot water. The column contains hot oil and a large number of Raschig rings.

7- Raschig rings: they are pieces of glass tube of the same diameter and length that are used in large number. The rings provide a large surface area within the volume of the column for holding the hot oil in the column for a period of time.

8- Vacuum measuring tube: it is a pressure meter for checking vacuum in the system.

9- Ventilation valve: it is the vacuum pump entrance valve.

10- Vacuum Pump: the main purpose of this pump is to reduce the pressure in a vessel or a closed system. A quantity of gas is removed from the system with each cycle of the pump.

11- 2nd column stage: it is the second column stage that is similar to 1st column stage described in section 6.

12- Collecting tank: it is a container that is used for storing mineral oil after degassing and dehumidifying.

13- Thermostat: it is a device for controlling the temperature of the system so that it is maintained near a desired set point temperature. For this study, the correct set point is 60°C.
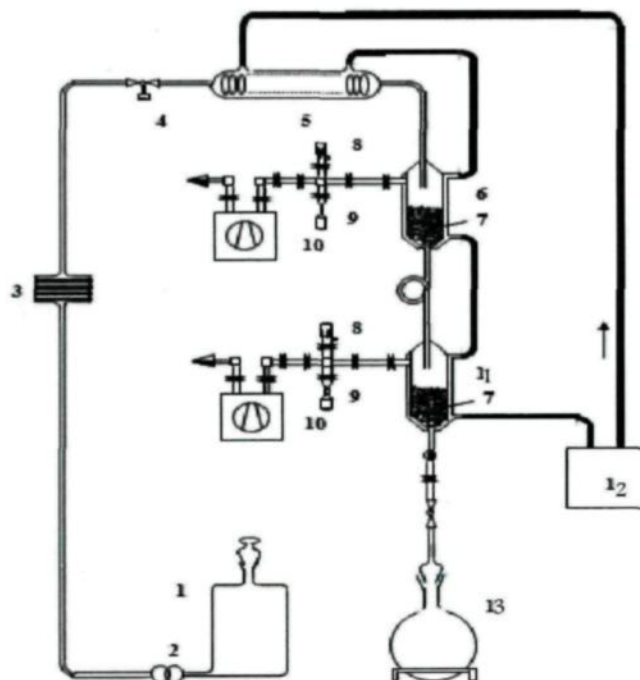

Figure 3.1. Two-stage drying and degassing unit developed at UQAC.

The aging procedure was performed by placing the oil samples in a convection oven (Figure 3.2) at 100°C for 200, 400, 600, 800, 1000, 1300, 1600 and 2000 hours with/ without air inlet.

Figure 3.2. Mechanical Convection (Model DKN-900).

Figure 3.3 provides an overview of the oil samples at specific aging periods.
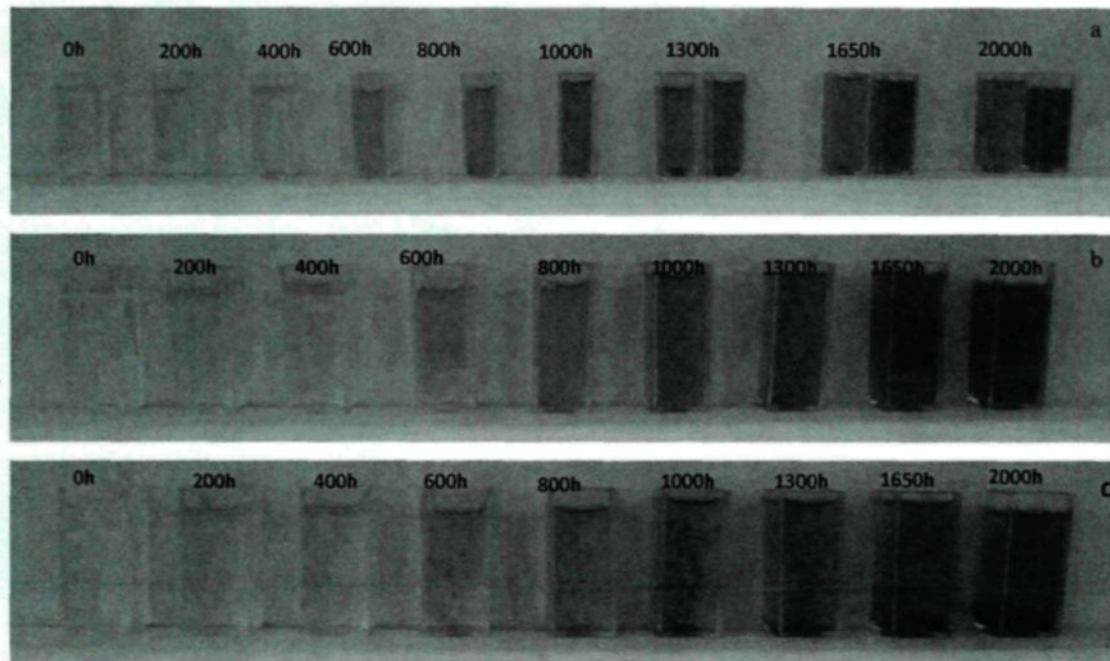

Figure 3.3. Overview of aged oil samples (a) the last three samples indicate aged oil after filtering and before filtering (b) aged oil samples before filtering (c) aged oil samples a few months after the aging process, after the product settled down at the bottom of the vessel

The color variation in transformer oil reflects the oil's degree of aging in the power transformer. New transformer oil is usually faint yellow. The progressive change in the color indicates that the transformer oil has deteriorated. This color change is essentially due to the oxidization of the oil in service, which subsequently leads to the formation of the acidic products. For each aging time, several parameters were examined. The aim of this research work is to find relationships between PDIV and the other physico-chemical parameters of oil and to find out how aging by-products affect each parameter.

3.2.1 Partial Discharge (IEC 61294)

In order to measure the partial discharge inception voltage (PDIV) by DDX 7000, a test cell was designed in our laboratory similar to the one used by Borsi [28]. It consists of a needle-to-plane gap, as shown in Figure 3.4 [57].

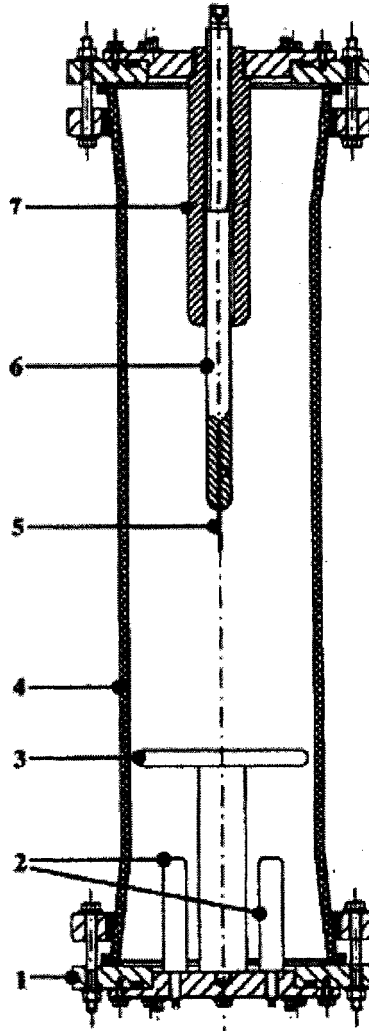**Figure 3.4.** Test vessel for determining the PD behavior of mineral oil. 1: Socket, 2: heater, 3: plate electrode, 4: glass cylinder, 5: point electrode, 6: holder for point electrode, 7: adjustment for point electrode [28].

Figure 3.5 shows the schematic diagram of the basic PDIV test circuit. Using a suitable voltage divider and a shunt resistance the applied voltage and current can be recorded.
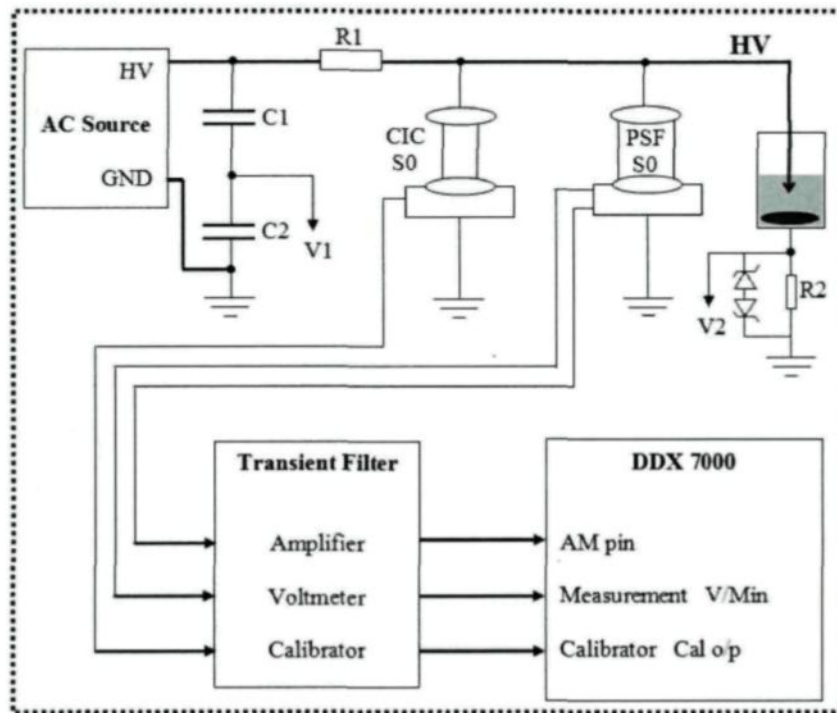
Figure 3.5. Schematic diagram of PD measurement

The following components can be found in the diagram above:

CIC: coupling capacitor (DDX 7000)

PSF=1200 (PF): voltage divider (DDX 7000)

R_1=100 (k Ω): current limiter

R_2 =50 (Ω): shunt resistance (for data acquisition)

C_1= 33.2 (μF) and C_2=9.4 (μF): voltage divider (for data acquisition)

V_1: Captured data to calculate the applied voltage

V_2: Captured data to calculate the current

Calibration procedure

The calibration goal is to confirm that the measurement system is able to correctly gauge the specified partial discharge magnitude. With the calibration of the measurement system in the complete test circuit, the scale factor for measuring apparent charge q was

determined. Calibration was performed for each new test object because such objects can influence calibration [58].

The calibration was carried out by injecting a short duration pulse of known charge magnitude q_0 into the terminals of the test object. Reading of the instrument at the given charge can be adjusted to create a reasonable scale factor for later partial discharge measurements. Calibration should be done for each measurement range used [58].

To guarantee duplication and equivalent PD measurements in IEC 60270, three basic measuring circuits are recommended, which differ by the arrangement of the measuring impedance Z_m [59, 60].

Real installation

Figure 3.6 shows the PD detector installation.
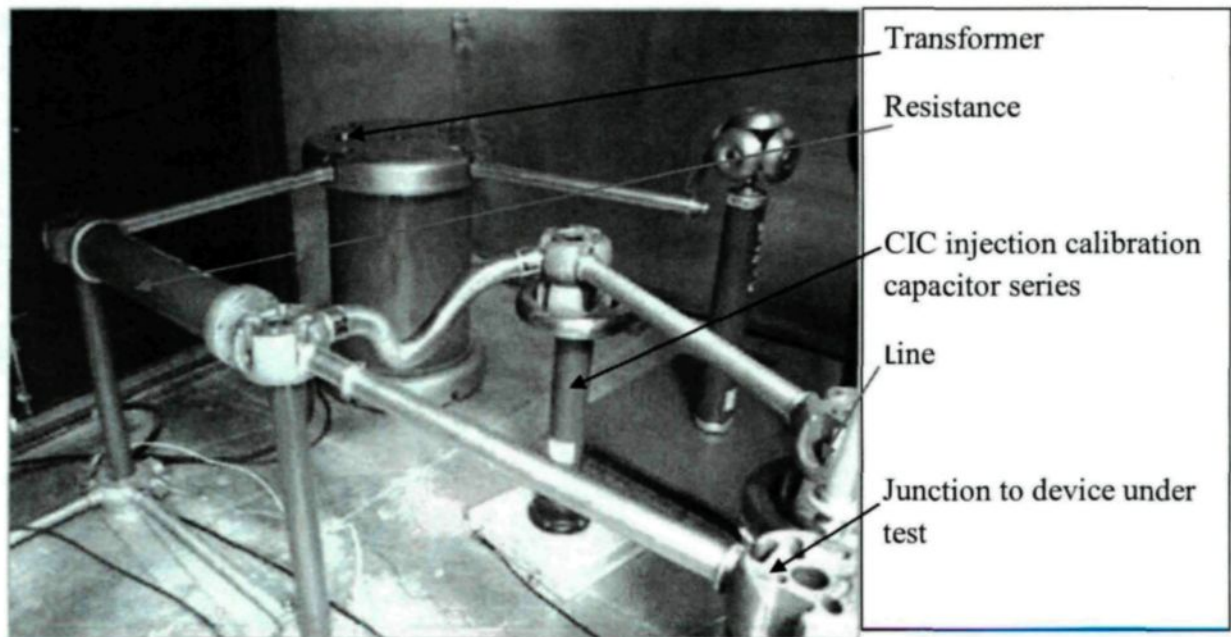
Figure 3.6. Overview of the experimental setup used to determine the PDIV.

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Partial discharge detector screen

Figure 3.7 shows an overview of the software screen that controls the calibration the device under the test. The PD pulse can be observed on the voltage pulse. The top section shows the maximum level of partial discharges and instantaneous voltage at any time.
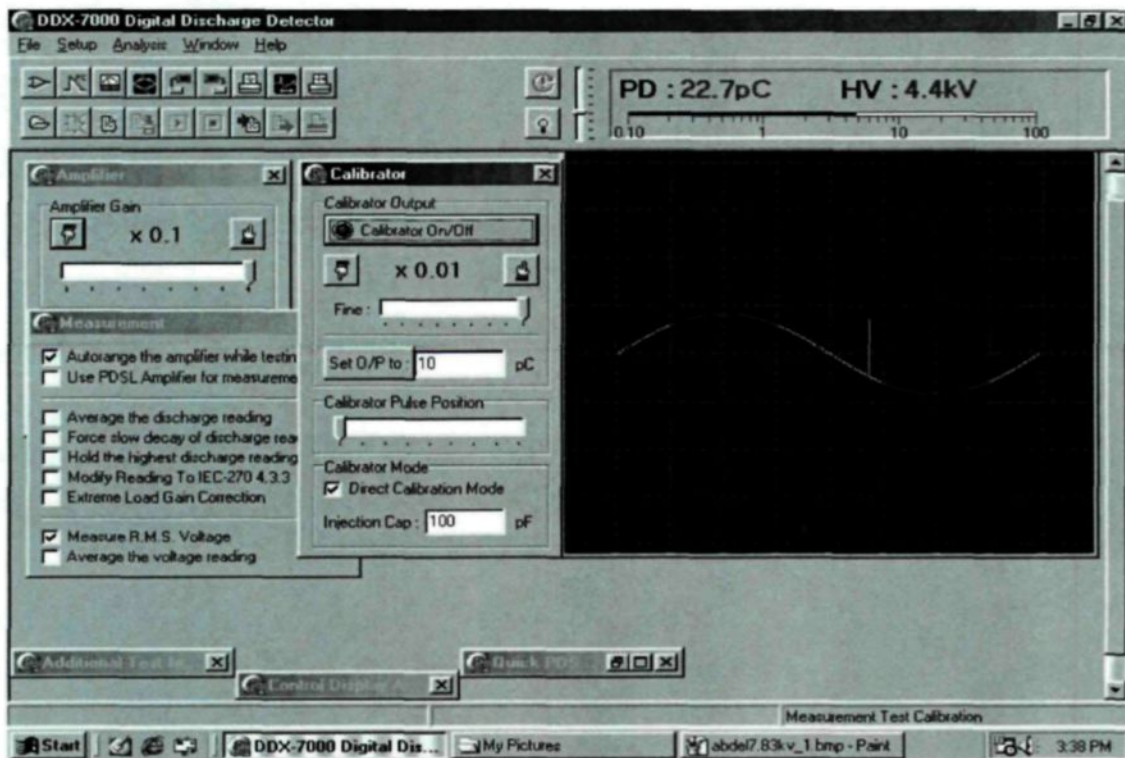
Figure 3.7. DDX-7000 software used in the PD detector instrument.

After completing the DDX calibration, the test procedure was started.

The test cell was cleaned, and a needle attached by adjusting three centimetres of air gap. To avoid the formation of air bubbles, oil was poured gently into the cell. The test cell stayed 15 minutes, and test started after connecting the cell to the high voltage terminal. Applied voltage was increased at a rate of 1 kV/s up to a 100 pC partial discharge level (as observed on the DDX7000).

These tests were repeated 10 times according to IEC 61294, with a five minutes delay between each two tests. After each test the cell was emptied and a new needle inserted. For a needle of 3-μm radius, the distance between the needle and the plane was changed; and the PDIV was measured 3 times with a 3-, 4- and 5-cm gap between the needle and plane [57].

The results of PDIV including the standard deviations, at different aging durations are illustrated in Figure 3.8.
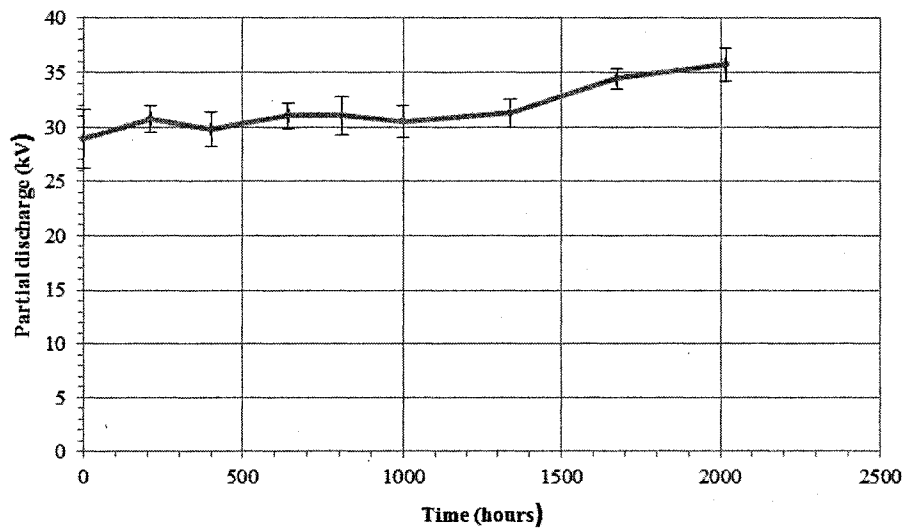
Figure 3.8. Partial discharge results of oil samples at different aging conditions.

In service, the insulation system is subjected to various stresses, including high temperature, vibrations, moisture, oxygen and other chemical contaminants. These stresses may lead to gradual degradation of the insulation system to the point that it can no longer withstand service voltage [15].

In most cases, insulating oil in operating equipment is hot. This high temperature completely changes the state of the insulating oil and all its liquid impurities. With a rise

in temperature, the mutual solubility of mineral oil components as well as the solubility of impurities in it increases sharply. The action of surface-active substances is reduced because they are dissolved in the insulating oil.

As illustrated in Figure 3.9 [61], even under normal service conditions, oil generates decay products. These impurities reduce the service reliability and shorten the life of transformers. Under these combined stresses, the chemical bonds of the molecules break down into free radicals. These free radicals may recombine and form other molecules that are no longer soluble in the oil. While large molecular weight particles cannot be dissolved in oil, smaller molecular weight particles are dissolved. Some of the charged particles may agglomerate into space charge and accelerated PDIV.
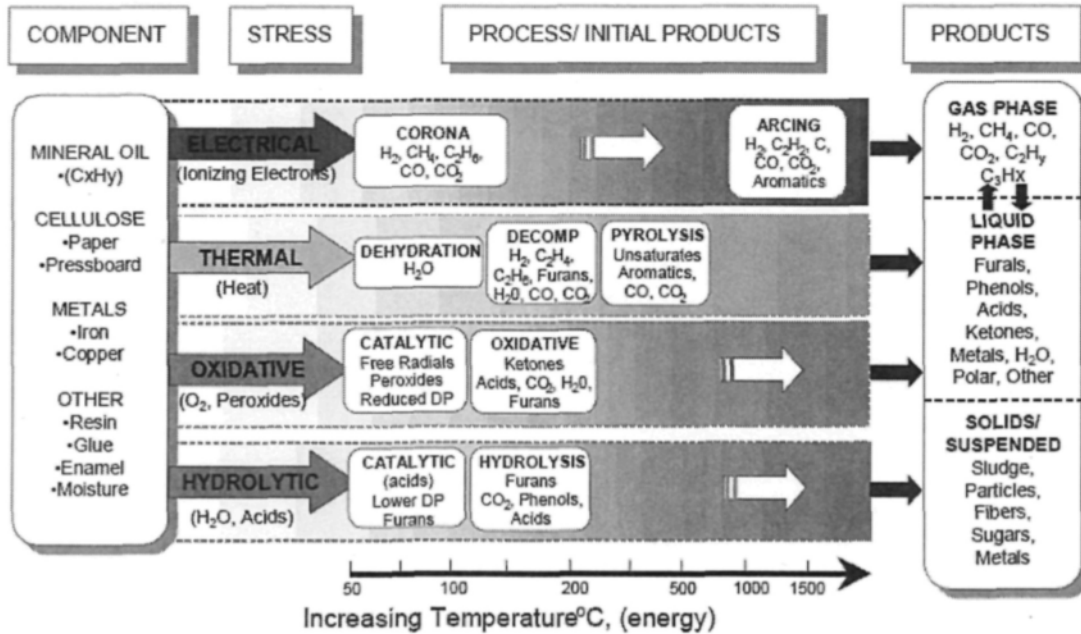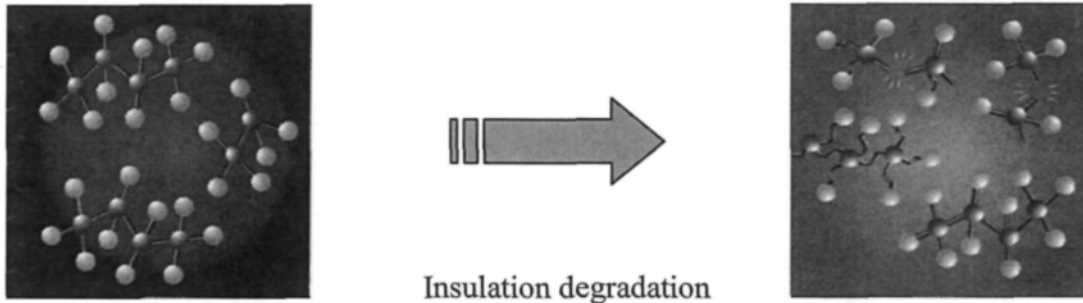

Insulation degradation

Figure 3.9. Simplified decomposition mechanism of transformer insulation.

The dominating an ageing product of oil oxidation contribution is made by carbonic acids. Carbonic acid and water can dissociate to ions and hence increase conductivity considerably [M. Koch, S. Tenbohlen, "Diagnostics of Oil-Paper-Insulations Using Relaxation Currents", Proceedings of the XIVth Int. Symp. on High Voltage Eng. (ISH), paper H-45, Beijing, China, August 25-29, 2005]:

$$H\text{-}COOH + H_2O \rightarrow H\text{-}COO^- + H_3O^+$$
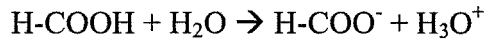
H-CO is the aldehyde group of a carbonic acid. According to M. Koch et al. [M. Koch, S. Tenbohlen, "Diagnostics of Oil-Paper-Insulations Using Relaxation Currents", Proceedings of the XIVth Int. Symp. on High Voltage Eng. (ISH), paper H-45, Beijing, China, August 25-29, 2005] only a combination of water and a dissociable substance will increase conductivity. Some authors found out, that water will not increase conductivity. It will anyway increase conductivity because of its self-dissociation, but this is hardly measurable. In a combination with a dissociable substance like acid the conductivity will increase considerably.

As shown in Figure 3.10(a), the electric field is modified in the presence of the space charge. The change in electric field may lead to field distortion at certain locations, causing localized breakdown and formation of voids. These voids can lead to further increases in the electric field of the nearby region leading to treeing phenomena and complete breakdown of the insulation.
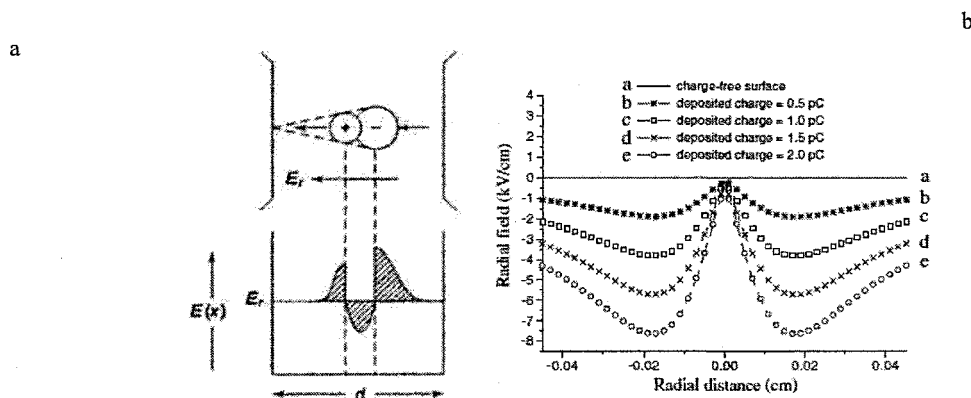

Figure 3.10. (a) Effect of space charge on electric field inside insulation, (b) Effect of surface charge on the radial field in the middle of the gap (r = 0.025 cm) in short air gaps [62].

Injecting charges of the same polarity as the voltage applied to the electrode, the electric field decreases in the region between the electrode point and the void and increases in the region between the void and the plane. Electric field around the electrode point first increases and then decreases as the charges first oppose the applied field. Therefore, when charges polarize in the electric field inside the plane to gap electrode, the electric field as a whole decreases while the risk of breakdown decreases. Figure 3.10(b) shows the effect of surface charge on the electric field in short air gaps. Curve (a) represents a charge-free surface and shows that by increasing the deposited charges, the electric field decreases as well as the risk of breakdown. Furthermore, PDIV increases in this situation.

PD Process in presence of space charge

A schematisation of a breakdown process in oil under AC voltage according to Dumke is shown in Figure 3.11 [63]. If some electronegative additives are injected, then these will later capture free electrons and form heavy negative ions, which move slowly. This is effective against the creation of electron avalanches, which may lead to an increase in flashover voltage. Increasing these additives can also increase the heavy negative ions, leading to the creation of negative ions concentrations between the positive space charge carriers and the electron cloud. The higher the concentration of negative ions, the higher is the probability a partial discharge channel forming between the positive space charge and the negative ion cloud [63].
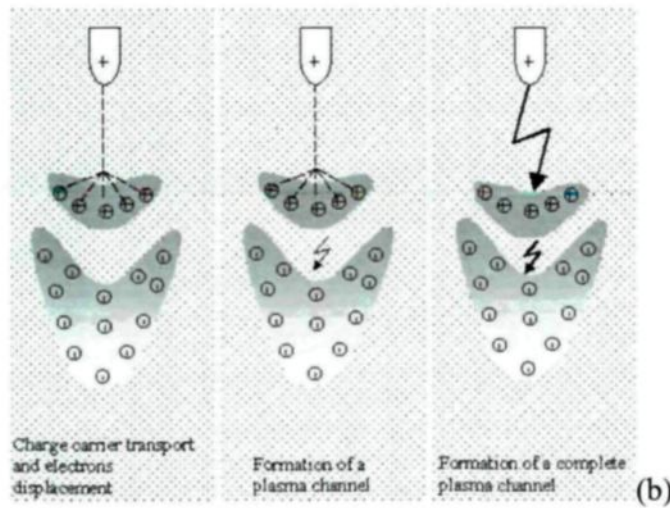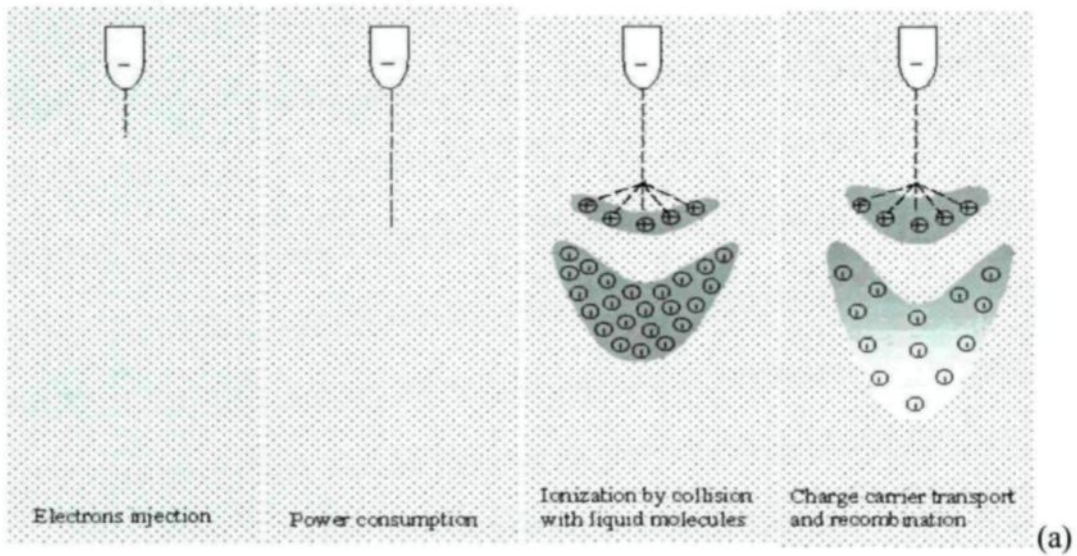
Figure 3.11. (a) Schematic representation of the discharge development through injection of a positive space charge into the negative voltage half wave [63]. (b) Schematic representation of the discharge development through injection of a negative space charge in the negative voltage half wave [63].
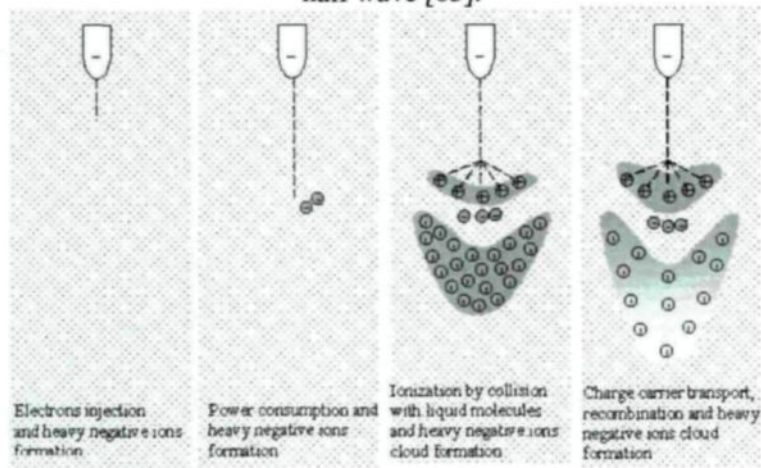
Figure 3.12. Schematic representation of the discharge development through injection of a positive space charge and formation of heavy negative ions in the negative voltage half wave[63].

3.2.2 Water content in oil and PDIV

As shown in Figure 3.13, the moisture content of transformer oil increases with aging. Oil samples in the oven deteriorate with time because of oxidation. As described in the literature review section, the water content in oil reaches the saturation point with increasing time.
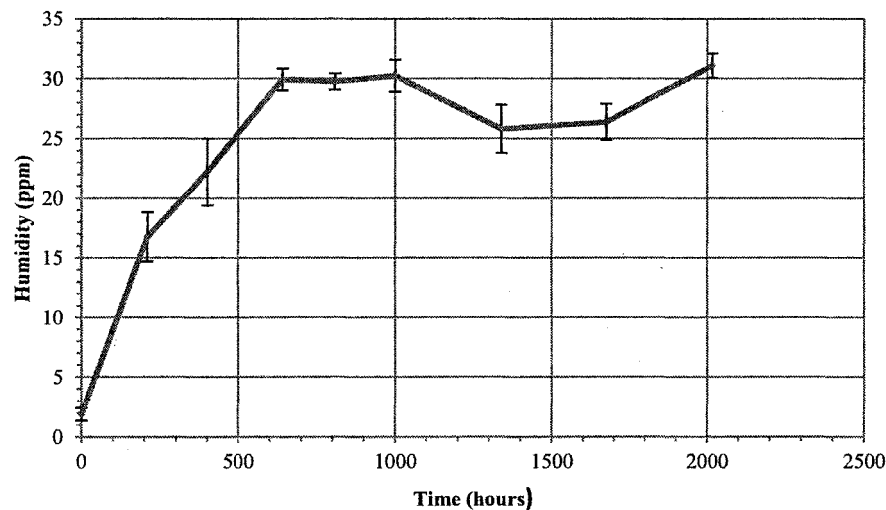
Figure 3.13. Water content results of oil samples at different aging conditions.

The correlation between PDIV and humidity content is reported in Figure 3.14. When humidity increase (as oil ages) to 13.89 %, then PDIV increase to 19%.

Coulometric titration by Karl Fischer represents a credible method to access the moisture content of insulation oil and paper/pressboard. However, oil additives and ageing products may interact with the Karl Fischer reagent, especially if direct titration is used [J. S. N'cho, I. Fofana, T. Aka-Ngnui and A. Beroual, "Effect of Exposure to Electrical Discharge on Transformer Oil Properties", International Journal of High Voltage Engineering, Vol. 37, No. 1, pp. 11507- 13, November 2011]. In other words, the

saturation limit of aged oil increases, thus impacting the physicochemical properties. At a given moisture content, aged oil sometimes show better breakdown strength when compared to new ones [J. S. N'cho, I. Fofana, T. Aka-Ngnui and A. Beroual, "Effect of Exposure to Electrical Discharge on Transformer Oil Properties", International Journal of High Voltage Engineering, Vol. 37, No. 1, pp. 11507- 13, November 2011].
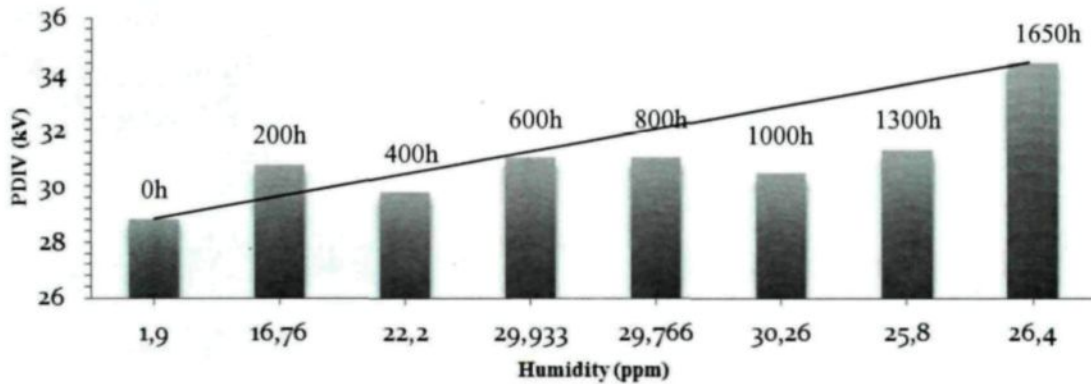
Figure 3.14. Correlation between PDIV and water content of oil samples at different aging conditions.

3.2.3 Acidity and PDIV

Total acidity is a key parameter, which can show the acid number in the oil. The acid existing in the new oil or formed in the aging oil leads to equipment damage. It reacts with metallic materials to create metal salts, which can act as catalyst in speeding up oil aging. To extend the service life of transformer oil and electrical equipment, monitoring of the total acid number in the oil is necessary [64].

As shown in Figure 3.15, the total acidity value is initially unchanged but begins to increase after 400 hours of aging. It indicates that the transformer oil deteriorates slowly at the beginning of aging and that few acidic products are formed. However, acidic products rise dramatically after 1200 hours of aging.

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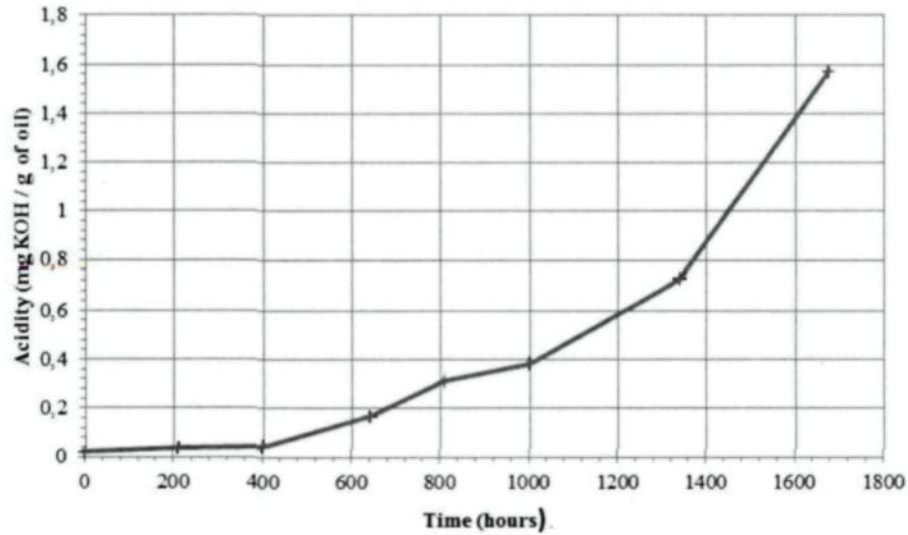
Figure 3.15. Acidity results of oil samples at different aging conditions.

Aging by-products, including acidity produced inside oil during the aging process, can increase the PDIV level. Acid produced during the aging process releases some particles and free radicals. These free radicals may recombine and form other molecules. These molecules cannot dissolve in the oil and act as space charges thus accelerating breakdown. Consequently, PDIV happens faster. Therefore, the more acidity, the more PDIV will occur.

The correlation between PDIV and acidity is illustrated in Figure 3.16. When acidity increases to 81.69 %, PDIV increases to 19%.
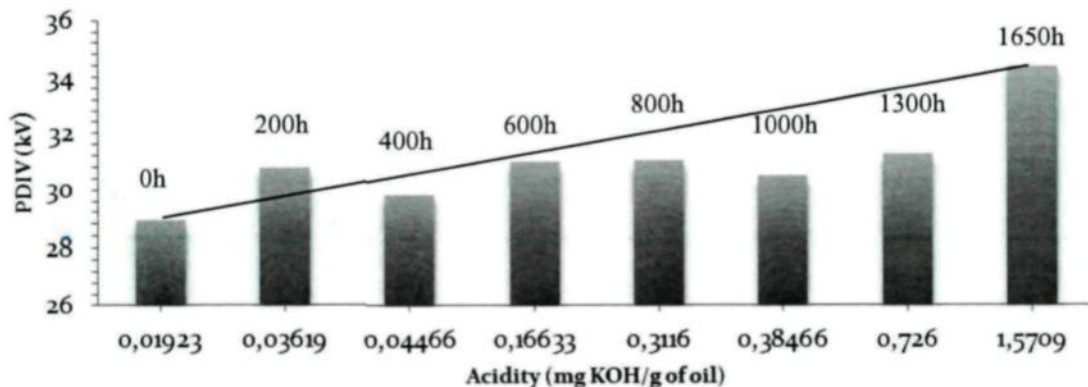
Figure 3.16. Correlation between PDIV and acidity of oil samples under different aging conditions.

3.2.4 Interfacial tension (IFT) and PDIV

Interfacial tension could show the degree of impurity of oil. Interfacial tension is very useful for detecting the presence of polar contaminants and oil aging products. New oil usually shows a high value of interfacial tension. Interfacial tension decreases with aging under the influence of combined stresses, oil oxidation, etc. The increase in oxidation contaminants causes a decrease in interfacial tension [64].

Figure 3.17 shows the variation of interfacial tension with time. The interfacial tension shows a large decrease of about 61.3 % for 1675 hours of aging time.
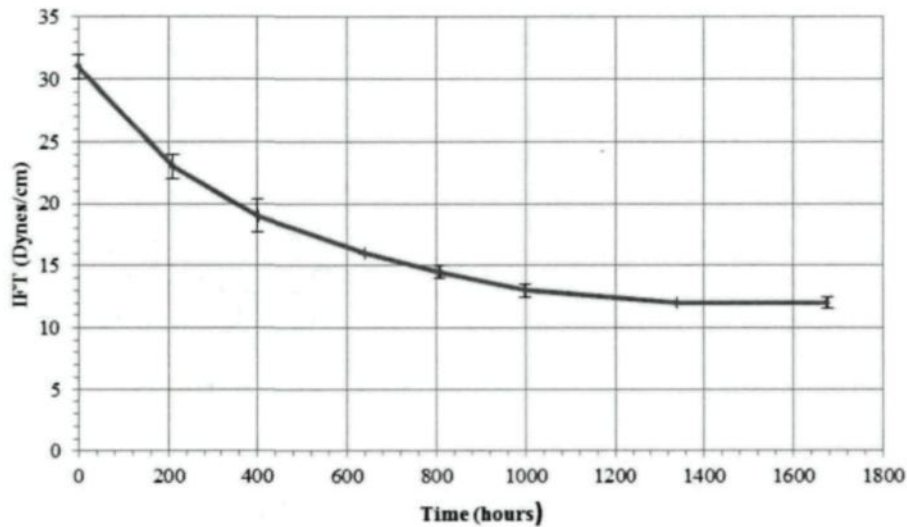
Figure 3.17. IFT results of oil samples at different aging conditions.

After the aging process, the impurities which exist inside oil cause a decrease of the tension needed to break the oil surface at oil-water interface. These impurities cause PDIV to increase. Consequently, the lower the IFT, the higher PDIV.

The correlation between PDIV and IFT is plotted in Figure 3.18. When IFT increases to 0.387 % , PDIV increases to 19%.

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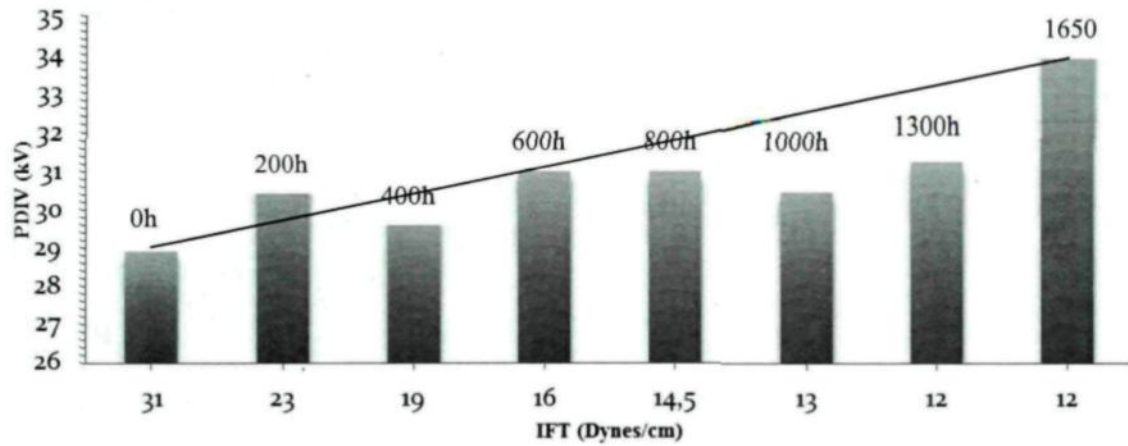
Figure 3.18. Correlation between PDIV and IFT of oil samples at different aging conditions.

3.2.5 Turbidity and PDIV

Turbidity is an optical characteristic or property of a liquid that generally describes the clarity or haziness of the liquid. As shown in Figure 3.19, increasing turbidity is due to the effect of suspended particulates as a result of aging. Turbidity experiences the largest change after 1675 hours of aging.
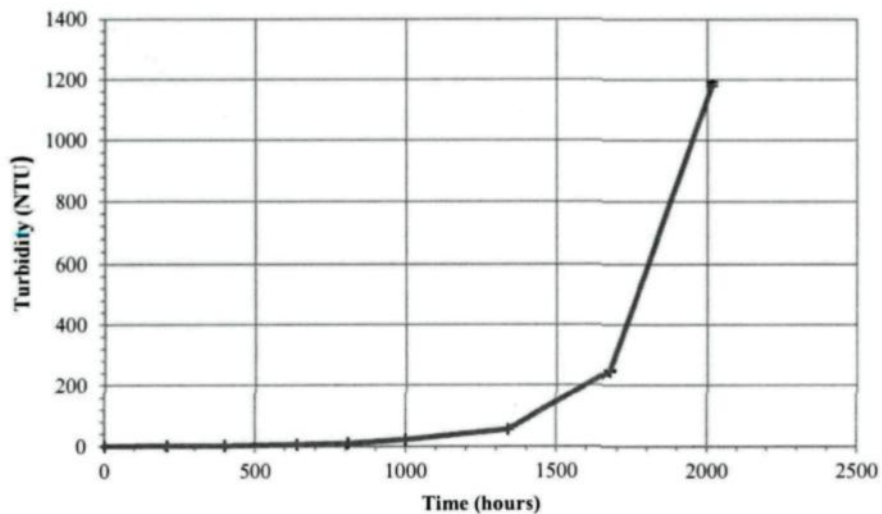
Figure 3.19. Turbidity results of oil samples at different aging conditions.

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The correlation between PDIV and turbidity is plotted in Figure 3.20. When turbidity increases to 447.27 %, the PDIV increases to 22%.
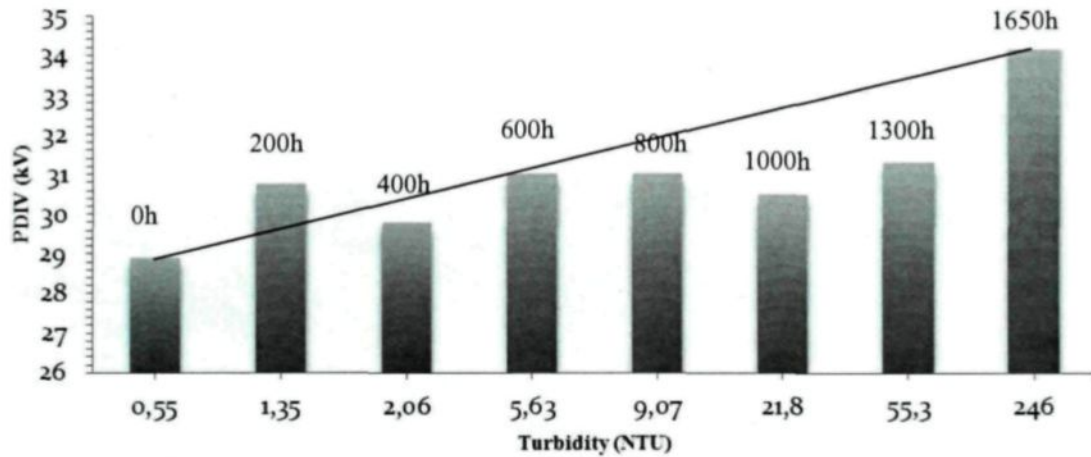
Figure 3.20. Correlation between PDIV and turbidity of oil samples at different aging conditions.

3.2.6 Dissolved Decay Product (DDP) and PDIV

Most of the by-products of decay that progressively damage the properties of oil insulation in power transformers result from secondary chemical reactions between decomposed molecules under the impact of electrical, chemical and thermal stresses [65]. UV-Spectrophotometer response is a test used to control the working of transformers and to provide information on their health that can be used for their maintenance.

Tests were carried out according to ASTM D-6802 to obtain the absorbance values of various samples of transformer oil. The absorbance curves were obtained from the instrument, which scans in the range of 360-600 nm. As shown in Figure 3.21, there is a relationship between the total amount of dissolved decay products in mineral insulating oil and the absorbance curve. An absorbance curve at the shorter wavelength shows that the oil is new. A shift under the longer wavelength shows increased amounts of the dissolved decay products in the oil. However, the shift of the absorbance curve to

the shorter wavelength after regaining used oil shows a decrease of dissolved decay products. Briefly, it shows the condition of the transformer oil.
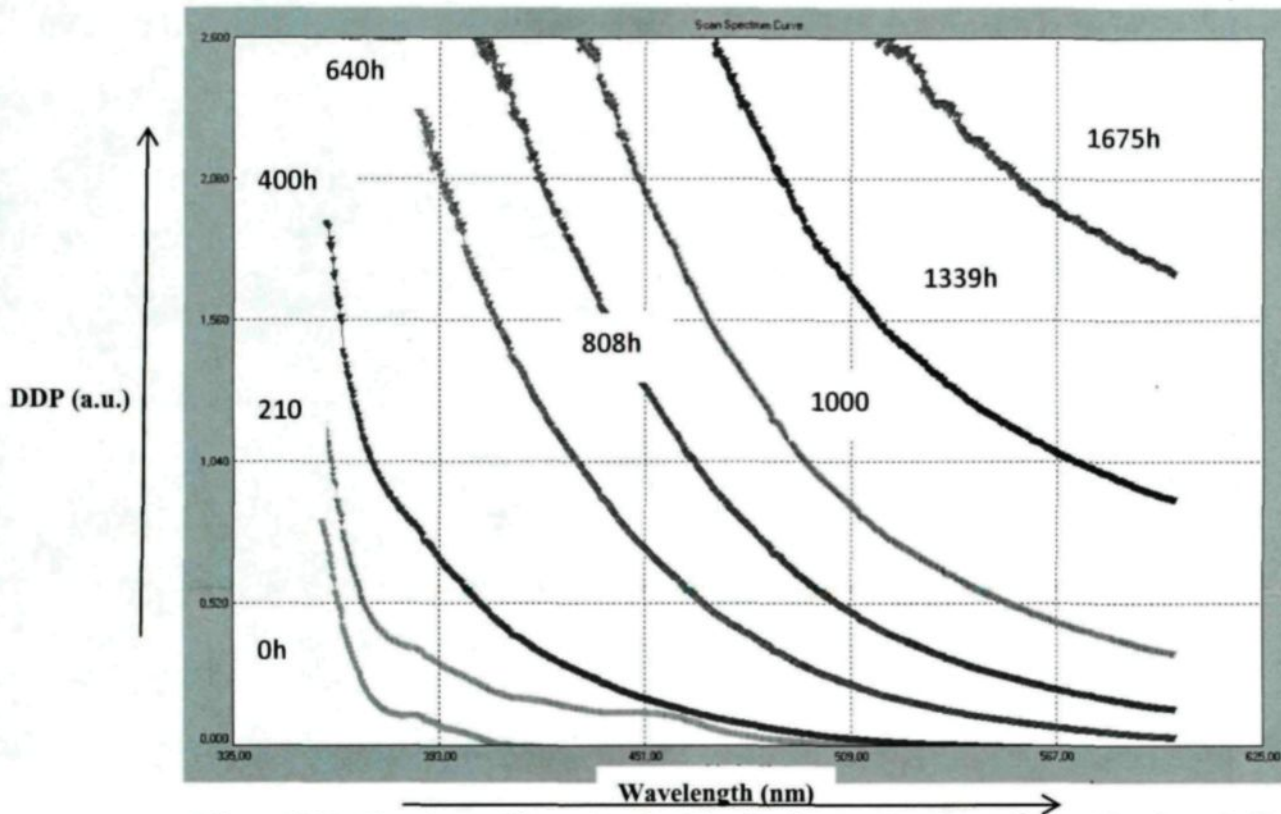
Figure 3.21. Absorbance illustrating the Dissolved Decay Products of new oil and aged oil.

It is obvious that the larger the amount of impurities in the oil, the higher the DDP and the partial discharge inception voltage are. Thus, aging by-products affect DDP directly; and the larger the DDP is, the higher the PDIV is.

3.3 Conclusions

At this stage of the research project, the aging procedure was performed by placing oil samples in a convection oven at 100 °C, for different time periods. Water content, acidity, DDP, IFT and turbidity tests were carried out for each sample. PDIV was measured for each sample. The relationships between these parameters at different

aging times were studied. It seems that the PDIV does not change much with aging except maybe for 1650 and 2000 hours and hardly correlate to any of the chemical parameters. Oxidation by-products (peroxide gas, water soluble acids, low molecular weight acids, fatty acids, water, alcohols, metallic soap, aldehydes, ketones, lacquers, sludges of asphaltene) change the chemical makeup of the oil to allow more water to be dissolved. During the aging process, the oil's colloidal state is destroyed in the formation of dispersed systems by impurities, particularly water. The insulating liquid tends to become an intrinsic solution.

PDs in insulating oils are intimately related to breakdown phenomena. PD inception and development is only possible when the insulating liquid starts to vaporize under the extra-rapid heating action of the electron's emission at the cathode. The associated energy is mainly related to the electric field at some "favourable sites." PDs in insulating are intimately related to breakdown, and are a consequence of electric field enhancement at the needle tip, where electron emission takes place. Generally speaking, aging by-products (impurities) dispersed in the insulating liquid do not reduce PD activity. Impurities are known to increase the water saturation limit, which, in turn, affects the breakdown process.

Chapter 4

Influence of nanoparticles on the dielectric properties of transformer oil

Chapter 4

Influence of nanoparticles on the dielectric properties of transformer oil

4.1 Introduction

Nanofluids are finding applications in a wide variety of industries, from transportation to power engineering, in microprocessors and in micro-electro-mechanical systems (MEMS), and in biotechnology. They consist of a base liquid in which nano-sized particles (1–100 nm) are suspended. The addition of nanoparticles can greatly improve the thermal and dielectric properties of the liquid, more specifically extending transformer lifespan and increasing loading/cooling capacity. The most commonly used nanoadditives include metals and metal oxides.

In this chapter, the breakdown voltage, permittivity and conductivity of mineral oil are investigated by the addition of TiO_2 nanoparticles to transformer oil. TiO_2 nanoparticles were selected because of their high permittivity and high thermal constant in comparison with other nanoparticles, such as ZnO, Al_2O_3, SiO_2, CuO, Fe_3O_4, ZrO_3, BN, $BaTiO_3$, AlN , etc. [6-8, 66].

Since the range of operating temperatures in Quebec varies between -50°C and +50°C, the investigations were performed at -47°C, -25°C, 0°C, 25°C and 47°C. For temperatures at or below 0°C, the tests were carried out in a climate chamber, while testing at above 0°C was performed in an oven.

Nanofluids were obtained by dispersion of nanoparticles in the base fluid through the ultrasonic route. The ultrasonic mixer sends out waves that produce heat. The number of encounters between nanoparticles intensifies when the temperature increases. These collisions may lead to agglomeration or recrystallization of nanoparticles.

4.2 Experimental setup

The goal of this investigation was to find the optimum concentration of nanoparticles that may help to improve the dielectric properties of the base oil.

Three dielectric characteristics, namely the dielectric constant, resistivity and breakdown voltage, were measured. These tests were repeated 3 times and the average value computed along with the standard deviation.

Furthermore, to understand how material structure and temperature affect the electrical properties of oil and oil-based nanofluids, investigations were performed at temperatures ranging from -47°C to 47°C covering temperature variations in cold climate regions.

4.2.1 Material preparation and dispersion

Material selection and preparation: The base oil used as matrix was Nynas mineral oil (Nytro 10XN) [67]. Important physical properties of transformer oil that make it an excellent electrical insulator and cooling medium are as follows: low density, high dielectric strength, high specific heat and thermal conductivity, together with low viscosity and pour point to provide effective heat transfer [68]. Other general characteristics of transformer oil are relative permittivity equal to $\varepsilon_r = 2.2$, resistivity greater than 1×10^9 Ω cm, and dielectric dissipation factor less than 0.001 at 60 Hz at 90°C [68].

Powder additives: TiO_2 nanopowder, white, Sigma Aldrich with, <100 nm particle size, 99.5% trace metals basis (Aldrich)[69].

Mixing and treatment: Five concentrations were considered, namely 0.001, 0.003, 0.005, 0.007 and 0.01 (g/ml).

Oil-based nanofluids were prepared according to the two-step method. The nanoparticles were dispersed in mineral oil by means of an ultrasonic and magnetic stirring method to obtain a homogenous nanofluid. The procedure for preparing the nanofluids included the following phases:

- Phase 1: Each sample was placed in ultrasonic apparatus for 60 minutes.
- Phase 2: Each sample was placed in stirring magnetic apparatus for 30 minutes.
- Phase 3: Each sample was replaced in ultrasonic apparatus for 30 minutes.

To allow the small micro-bubbles that were produced during sonification to move to the surface, the suspensions were left for two hours before any measurements were taken. After the nanofluid preparation, no extra treatment was given.

4.2.2 AC breakdown voltages assessment

In general, the AC breakdown voltage test is the main way of assessing the liquid's ability to bear electric stress at power frequency [40].

The AC breakdown voltage test was carried out with a 60 Hz AC voltage at room temperature with the Oil Tester DTA 100 C [70]. The standard liquid dielectric cell required the use of a plane-to-plane electrode configuration with a 2.5 mm gap spacing (according to the IEC 60156 Standard). The voltage rise rate was set to 2 kV/s.

The oil samples were prepared with five nanoparticle concentrations (0, 0.003, 0.005, 0.007 and 0.01 (g/ml)).

The results of the AC breakdown voltage tests for the mineral oil and mineral oil-based nanofluids with different concentrations are plotted in Figure 4.1.
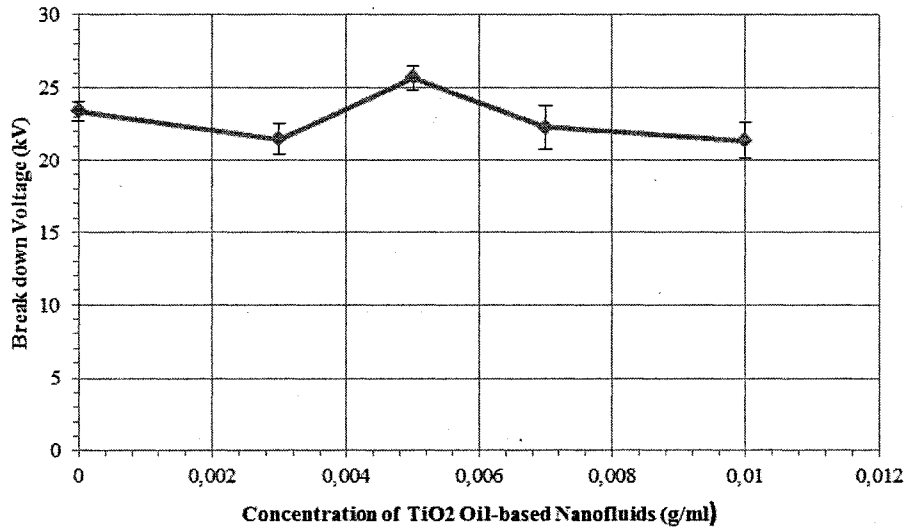
Figure 4.1. Comparison of AC breakdown voltages for different concentrations of mineral oil-based nanofluids and mineral oil.

As shown in Figure 4.1, the breakdown strength increases from 23.4 (kV) to 25.7 (kV) for a concentration of 0.005 (g/ml). When the concentration is further increased, the breakdown voltage is inclined to decrease. This might be caused by the agglomeration of TiO_2 particles with a concomitant reduction in breakdown voltage. The value of breakdown voltage is decreased in the concentration of 0.003 (g/ml); this quantity is acceptable because it is within the range of the standard deviation. Thus, the value of breakdown voltage is close to the breakdown voltage value in pure mineral oil.

The results showed that the breakdown voltage of mineral oil was improved with addition of TiO_2 nanoparticles at a concentration of 0.005 (g/ml). This finding could be explained by the fact that the polarized TiO_2 nanoparticles can acts as electron traps to catch the free electrons released from oil molecules under high electric field and that would otherwise cause breakdown. It could also be related to the higher chance of electron scattering in nanofluids due to the high specific surface area of nanoparticles. Therefore, adding TiO_2 nanoparticles to base oil can improve breakdown voltage when at the optimum concentration.

As explained before, the optimum concentration considered in the subsequent investigations is derived from the AC breakdown test in ambient temperature. The preceding investigations were performed in the temperature range varying from -47°C to 47°C. Five different points were selected, namely, -47°C, -25°C, -0°C, 25°C, +47°C to measure the three characteristics of breakdown voltage, resistivity and dielectric constant.

The result of breakdown voltage, resistivity and dielectric constant tests for pure mineral oil and mineral oil-based TiO_2 nanofluid are shown in Figures 4.2, 4.3 and 4.4, respectively.

4.2.3 Effect of temperature and nanoparticles on breakdown voltage

The results of AC breakdown voltage tests for pure mineral oil and mineral oil-based TiO_2 nanofluids, with a concentration of 0.005 (g/ml) at temperatures ranging from -47°C to 47°C, are plotted in Figure 4.2.
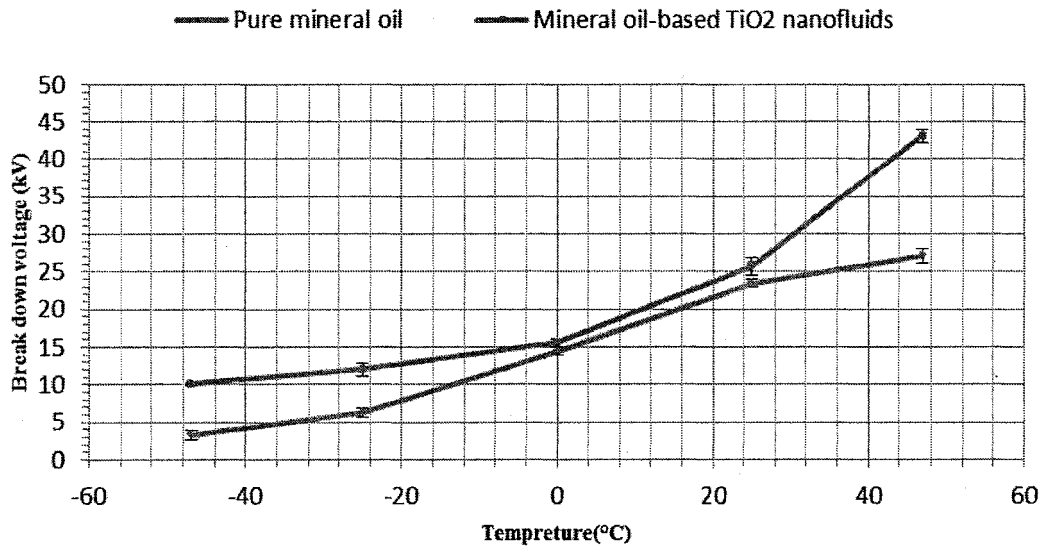
Figure 4.2. Comparison of AC breakdown voltages for pure mineral oil and mineral oil-based TiO_2 nanofluids with concentration 0.005 (g/ml) at temperatures ranging from -47°C to 47°C.

Effect of temperature on breakdown voltage

As shown in Figure 4.2, the breakdown voltage increases in both pure mineral oil and mineral oil-based TiO_2 nanofluids when the temperature increases. The moisture content of the oil samples was measured at about 20 ppm.

It must be pointed out that the AC breakdown voltages U_B are strongly temperature dependent. The lower the temperature, the lower the breakdown voltage is. The reason for the relationship is the water saturation limit. At a certain temperature mineral oil can hold a certain amount of water. If the water content is higher than this saturation limit the breakdown voltage strongly decreases. Additionally, the saturation limit is temperature dependent. It decreases with a lower temperature. The saturation limit for the investigated mineral oil at 20°C is about 50 ppm, but at 0°C this limit goes down to only about 15 ppm. At the latter temperature, a specimen with a water content of e.g. 20 ppm would, therefore, contain free water, thus lowering U_B.

Effect of nanoparticles on breakdown voltage

As shown in Figure 4.2, adding TiO_2 nanoparticles in mineral oil at temperatures ranging from -47°C to +47°C causes breakdown voltages to increase. This is explained as follows. Electronegativity is a measure of the affinity of an atom for electrons in a covalent bond. The higher the position of an atom in the periodic table, the greater the electronegativity is. Thus, Ti has high electronegativity because Ti is located in a high position of the table.

The definition of electronegativity can be also extended to the oxides of elements [11]. Consequently TiO_2 nanoparticles are inclined to trap electrons and catch the free electrons released from oil molecules under high electric field that would otherwise cause breakdown. The result is that the breakdown voltage increases.

4.2.4 Effect of temperature and nanoparticles on resistivity

Volume resistivity is measured by applying a known voltage to the opposite side of an insulator sample. The current is furthermore measured and the resistance measured from Ohm's law. From the resistance measurement, the resistivity is calculated based on the physical dimensions of the test sample. The resistivity depends on several factors. First, it is a function of the applied voltage. Sometimes the voltage may be varied with the aim of controlling an insulator's voltage dependence. The resistivity also varies as a function of the length of electrification time. The longer the voltage is applied, the higher the resistivity because the material continues to charge exponentially. Environmental factors can also affect an insulator's resistivity [71]. To make accurate comparisons to a specific test, the applied voltage, electrification time, and environmental conditions should be kept constant from one test to the next. According to the ASTM D257 Standard [72], a commonly used test condition is a voltage of 500 V applied for 60 seconds.

Model Keithley 6517A automatically performs the following calculations and shows the volume resistivity. The cell was cylindrical in shape. The geometry of the cylinder is: height= 6.2 (cm), radius= 21.35 (mm). The resistivity was computed as follow :

$$\rho_v = \frac{K_v}{\tau} R$$

ρ_v= volume resistivity

k_v= the effective area=83.17 (cm)

τ= average thickness of sample= 3.5 (cm)

R= measured resistance in ohms (V/I)

The inverse of resistivity is conductivity: Electrical conductivity =σ=1/ρ.

The results of resistivity tests for pure mineral oil and mineral oil-based TiO_2 nanofluid at temperatures ranging from -47°C to +47°C are plotted in Figure 4.3.
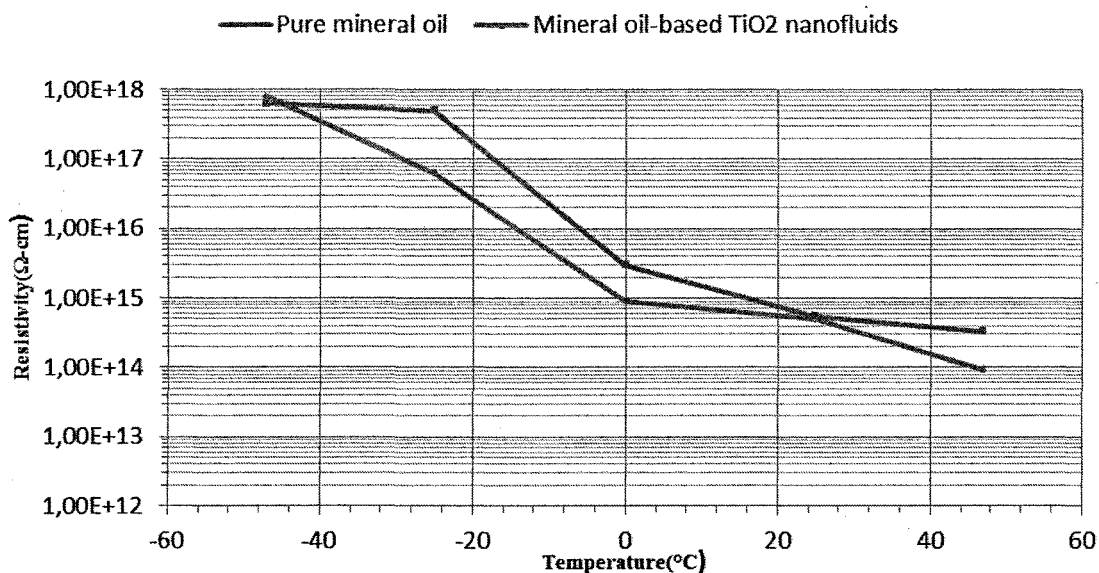
Figure 4.3. Comparison of resistivities for pure mineral oil and mineral oil-based TiO2 nanofluid at temperatures ranging from -47°C to 47°C.

Effect of temperature on resistivity

As shown in Figure 4.3, with an increase in temperature the resistivity decreases in both pure mineral oil and mineral oil-based TiO_2 nanofluids. Changing temperature alters the resistivity of material by changing the activity of atoms within the material.

Materials are classified in two general groups: conductors and insulators. The resistivity of conductors increases at higher temperatures, but the resistivity of insulators decreases at higher temperatures. These changes in resistivity occur because of the movement of electrons from one atom to another in an electric field. As explained before, every material has two bands, the valence band and the higher energy conduction band. The electrons in the conduction band are free electrons that migrate easily from one atom to another under electric field. The electrons in the valence band are restricted electrons, which strongly stick to the core of the atom. Atomic structure of a material is affected by increases in temperature such that the atoms vibrate and the higher the temperature, the more rapidly they do so.

In a conductor, there are many free electrons so that many collisions occur between the restricted electron and the free electrons due to the vibration of the atoms. On the other hand, an insulator contains so few free electrons that they barely vibrate at all. Virtually all of the electrons remain within their specific atoms, and current flow is negligible. Heating an insulating material causes atoms within an insulator to vibrate, so if the atoms gain enough heat, they vibrate sufficiently to shake some of their restricted electrons free and cause free electrons to become carriers of current. This leads to decrease resistivity because resistivity is considered as flow of current within a material [73].

However, the opposite process is happened in cooling an insulating material. Cooling an insulating material leads to a decrease in atom vibrations within the insulator and fixes them in place. Hence hardly any current can flow within the insulator, and resistivity increases.

Effect of nanoparticle on resistivity

As described before, an insulator contains so few free electrons that they almost cannot move. Virtually all of the electrons are surrounded within their specific atoms and almost no current can flow. TiO_2 nanoparticles have a high dielectric constant and electron affinity that is inclined to trap electrons and catch the free electrons released from mineral oil molecules. This behavior decreases the amount of free electrons in mineral oil and results in a slight decrease of the flow of current in mineral oil. Conversely, resistivity increases when TiO_2 nanoparticles are added to mineral oil.

According to the formula $R=\rho.(L/S)$, enhancing the resistivity value results is enhancing the resistance value. Then according to the formula $I=V/R$, enhancing the value of R results in decreasing I (leakage current). So, to have a good insulator, the leakage current should be low.

All these results confirm that adding nanoparticle TiO_2 to mineral oil holds promise for improving its insulating properties. Therefore the objective of this research project has been attained.

4.2.5 Effect of temperature and nanoparticle on dielectric constant

The Novocontrol Beta advanced impedance analyser was used to measure the dielectric characteristics from frequency range: 3 μHz to 20 MHz. The same cell as that of the resistivity tests was used.

The capacitance between the plates (C_p') is automatically measured with Novocontrol. The relative permittivity (ε_r') or k which is the ratio of the capacitance of sample (C_p') to the capacitance of the empty cell (C_0) was calculated as follows:

$$\varepsilon_r' = k = C_p'/C_0 = \varepsilon/\varepsilon_0$$

The results of dielectric constant tests for pure mineral oil and mineral oil-based TiO_2 nanofluid at temperatures ranging from -47°C to +47°C are plotted in Figure 4.4.
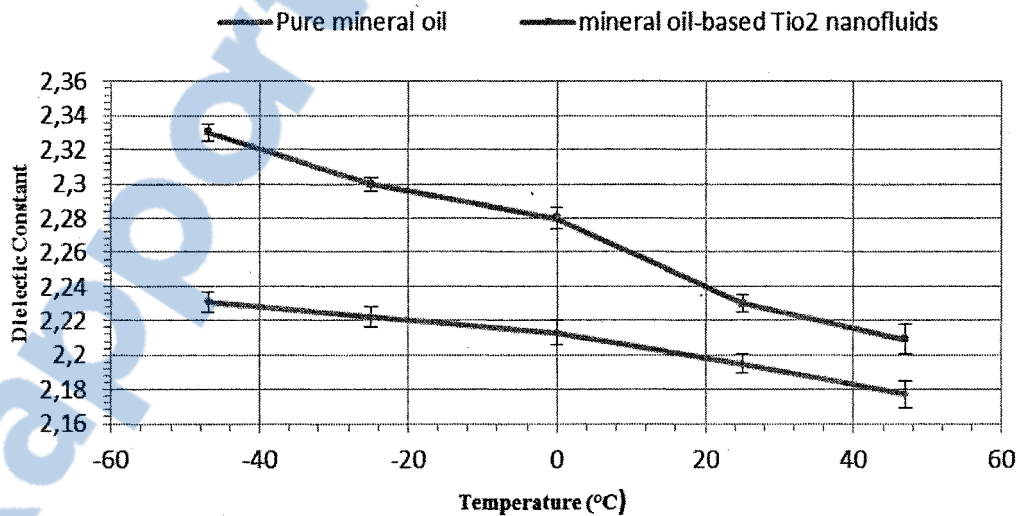

Figure 4.4. Comparison of dielectric constants for pure mineral oil and mineral oil-based TiO_2 nanofluid at temperatures ranging from -47°C to 47°C.

Effect of temperature on dielectric constant

The molecules in insulation fluid are always in random movement because they own some energy. After applying an electric field to the insulation fluid, molecules rotate and arrange themselves in a line with the field. When temperature is increased, the molecules gain more thermal energy, so that the random thermal movements intensify. Hence, the molecules are no longer aligned with the electric field and the polarization of materials is reduced with resulting decrease in dielectric constant. However, thermal energy is lost as temperature decreases. Therefore the thermal movements along with the energy owned by molecules are reduced. To sum up, after applying an electric field, the molecules are better aligned with each other and the electric field; consequently, the material becomes more polarized and the dielectric constant increases.

Effect of nanoparticles on dielectric constant

As shown in Figure 4.4, adding TiO_2 nanoparticles in mineral oil at temperatures ranging from -47°C to +47°C causes dielectric constants to increase. As already described, materials that own more accessible polarisation mechanisms have higher dielectric constants. For example, materials with permanent dipoles have higher dielectric constants than similar non-polar materials. TiO_2 molecules have high dielectric constants because of their polar structure, which consists of permanent dipoles [74, 75].

When nanoparticles with high dielectric constants like TiO_2 are added to mineral oil, the TiO_2 molecules place themselves between mineral oil molecules. The mineral oil molecules always are in random motion because they own some energy. After applying an electric field to mineral oil, the molecules rotate and arrange in a line with the field. After adding TiO_2 nanoparticles, its atoms tend to catch mineral oil electrons and decrease the energy of the mineral oil molecules. Consequently, the molecules are more aligned with each other and the electric field, so that the material is more polarized and, hence, the dielectric constant increases. On the other hand, TiO_2 molecules have high dielectric constants and polar structure (permanent dipoles) whose pole changes when a field is applied such that they rotate and arrange in a line with the field.

Furthermore, the high dielectric constant of TiO_2 nanoparticles results in its ability to polarize in an applied field. Hence nanoparticles near or on the surface of a cathode increase the local electric field and act as field enhancement [41].

Considering the oil-paper transformer of Figure 4.5, oil is mixed with paper inside the transformer. It could be considered as two capacitances in parallel, the first one filled with oil and the second one filled with paper. Since $E_{oil} = (\varepsilon_{paper}/\varepsilon_{oil}).E_{paper}$, any increase in oil dielectric constant (ε_{oil}) will make the electric field inside oil (E_{oil}) decrease and the breakdown risk to decrease as well. All these results confirm that adding TiO_2 nanoparticles to mineral oil hold promises for improving its insulating properties. Therefore, the objective of this research project has been attained.
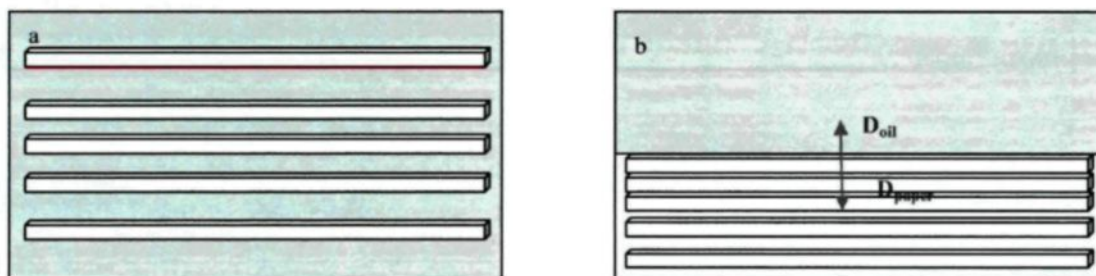
Figure 4.5. Simplified schematic of: a) oil + paper capacitor, b) oil capacitor in parallel with paper capacitor.

4.3 Summary

In this chapter, the breakdown voltage, permittivity and conductivity of mineral oil reinforced with TiO_2 nanoparticles were measured. The effect of adding TiO_2 nanoparticles on the dielectric characteristics of mineral oil was assessed at five different temperatures. It was observed that TiO_2 can be used as an additive to the mineral oil used in electrical power transformers and other oil-cooled electrical equipment to enhance the dielectric properties of the oil without compromising its required electrical insulation properties, in such a way that failures are suppressed, oil life is greatly extended and load boundaries are elevated. The optimal concentration of TiO_2 is 0.005 g/ml.

Chapter 5

Conclusions and Recommendations

Chapter 5

Conclusions and recommendations

5.1 Conclusions

Partial discharge is known as a harmful degradation process for electrical insulation. The properties of insulating liquids are influenced by aging processes. Natural aging is caused by electrical and thermal stress, while various parameters, such as metallic components and oxygen, act as catalysts. Since by-products of aging affect the physico-chemical parameters (acidity, IFT, turbidity, moisture constant, DDP, etc.), correlations between each parameter and partial discharge inception voltage were investigated. The objective of this series of tests was to determine the contaminants inside the new and aged oil samples submitted to electrical, thermal and chemical stresses composition to demonstrate that keeping oil in the virgin condition is necessary for a longer transformer lifespan. From the investigations, it may be conclude that partial discharge (PDs) in insulating oils are intimately related to the breakdown phenomena and PD inception and development is only possible when the insulating liquid start to vaporize under the extra rapid heating action of the electron's emission at the high voltage electrode. The associated energy is mainly related to the electrical field at some "favourable sites". More in general, impurities dispersed in the insulating liquid or some difference in its chemistry doesn't influence the PD's activity in a detectable manner.

TiO$_2$ nanofiller was investigated with the objective of enhancing the dielectric performance of mineral oil when used within power system equipment. The strength of nanocomposites is highly dependent on how well the particles are dispersed in the matrix since large internal microscopic interfaces between the fillers and the molecules of the material are expected to substantially improve the properties of the nanocomposite. Otherwise, the resulting materials would possess properties similar to conventional

composites modified with microfillers. Hence, one of the critical issues in the field of nanofluids is to assure the uniform dispersion of nanofillers in the matrix, as was addressed in this study.

A comparison of breakdown properties, dielectric constant and resistivity between mineral oil and nanofluids at temperatures ranging from -47°C to +47°C was carried out. It was found that breakdown voltages, dielectric constant and resistivity under power frequency conditions were improved for specific compositions. The enhancement of breakdown strength of transformer oil-based nanofluids is mainly attributed to the dielectric properties of TiO_2 nanoparticles that may act as electron traps in the process of electron transfer within electrically stressed nanofluids. These results confirmed that transformer oil modified with TiO_2 nanoparticles holds promise for improving its insulating properties.

5.2 Recommandations

The use of nanofluids in a wide variety of applications, including power transformers, appears promising. However, the development of the field is hindered by (i) lack of agreement of results obtained by different researchers; (ii) poor characterization of suspensions; (iii) lack of theoretical understanding of the mechanisms responsible for changes in properties. Therefore, several important issues should receive greater attention in the near future.

1) TiO_2 nanoparticles are currently used in this project. However, exploration of new materials or other nanoparticles, such as other metal oxides (ZnO, SiO_2, MnO_2, etc.) with better performance is still booming.

2) The development of new insulating fluids based on the incorporation of nanoparticles to enhance characteristics, such as dielectric performance, heat transfer capability, low temperature pour point, and resistance to oxidation.

3) Preparation of homogeneous suspension remains a technical challenge since the nanoparticles tend to form aggregates due to very strong van der Waals interactions. Addressing this important issue will guarantee long-term applications.

4) Transformer cooling is important to the power generation industry, especially when the objective is to reduce transformer size and weight. It is therefore important to assess how nanoparticles might affect the thermal properties of oil. The ever-growing demand for greater electricity production can lead to the necessity of replacing and/or upgrading transformers on a large scale.

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