Electro-Insulating Nanofluids Based on Synthetic Ester and TiO$_2$ or C$_{60}$ Nanoparticles in Power Transformer

Zbigniew Nadolny * and Grzegorz Dombek

Institute of Electric Power Engineering, Poznan University of Technology, Piotrowo 3A, 60-965 Poznan, Poland; grzegorz.dombek@put.poznan.pl
* Correspondence: zbigniew.nadolny@put.poznan.pl; Tel.: +48-61-665-2298

Received: 13 June 2018; Accepted: 24 July 2018; Published: 27 July 2018

Abstract: The article discusses thermal properties of synthetic ester admixed with nanoparticles. The analyzed thermal properties were: thermal conductivity $\lambda$, kinematic viscosity $\nu$, density $\rho$, specific heat $c_p$, and the thermal expansion factor $\beta$ - all obtained by means of measurements. On the basis of these, the authors calculated the heat transfer factor $\alpha$, which determines the ability of the liquid to heat transport. The authors used nanoparticles of fullerene C$_{60}$ and titanium oxide TiO$_2$. The analysis of the thermal properties was done for the temperatures of 25, 40, 60 and 80 $^\circ$C. The authors analyzed the impact of nanoparticles C$_{60}$ and TiO$_2$ on thermal properties of synthetic ester. They proved that fullerene C$_{60}$ in principle had no influence on heat transfer factor $\alpha$ of the ester, while titanium oxide TiO$_2$ had some positive influence on the factor, the value of which increased about 1–3%.

Keywords: synthetic ester; titanium dioxide; fullerene; nanofluids; dielectrics; insulation system; power transformer; thermal properties

1. Introduction

In addition to electrical insulation, one of the main functions of the electro-insulating liquid, filling the inside of the transformer, is to transport heat outside the device. The heat transport goes along the following way: heat source $\rightarrow$ paper impregnated with electro-insulating liquid $\rightarrow$ electro-insulating liquid $\rightarrow$ tank $\rightarrow$ surrounding [1,2]. Because the liquid fills a substantial space inside the device it is vitally important in the process of heat transport [3]. In the case of liquids, this transport is connected with the effect of transferring heat by liquid and it is determined on the basis of the heat transfer factor $\alpha$. This factor depends on a number of thermal properties of the electro-insulating liquid [4,5].

Synthetic esters are mainly applied in distribution transformers, in the place of previously used mineral oils (the most popular electro-insulating liquid for last hundred years) [6]. They can also be used in places where dry transformers had been used so far in densely populated areas or near water reservoirs. Synthetic esters are also a good alternative to silicone oils and PCBs. However, lately they have been used more and more often in power transformers [7,8]. This can be affected by synthetic esters properties, such as breakdown voltage, electric permittivity, biodegradability, and flash point [9].

Breakdown voltage of synthetic esters is comparable to breakdown voltage of mineral oil (the level of about 70 kV). We should note, however, that during the transformer operation the liquid filling undergoes the process of moistening. Increased ability of esters to adsorb water, resulting from their polar composition [10], results in the fact that with the progress of the moistening process, breakdown voltage of ester is higher than the breakdown voltage of mineral oil [7].

Electric permittivity of synthetic ester ($\varepsilon = 3.2$) is higher than electric permittivity of mineral oil ($\varepsilon = 2.2$). Electric permittivity of ester is close to the permittivity of paper ($\varepsilon = 4$), therefore, distribution
of electric field intensity for the paper-synthetic ester system will be more uniform. This results in lower electric field intensity in electro-insulating liquid, and thus it reduces the probability of breakdown in the liquid. It is vital because electro-insulating liquids are characteristic of lower electric strength in reference to impregnated transformer paper [11].

The increase of interest in synthetic esters is undoubtedly influenced by their environmental and fire protection properties. Some synthetic esters are nearly 90% degradable, whereas mineral oil is hardly 10%. In addition, the flash point of most synthetic esters is significantly above 200 °C—in some cases it reaches 275 °C. This means that the flash point of synthetic esters is significantly higher than the flash point of mineral oils (about 150 °C) [7,12].

Lately, more and more attention has been paid to special kinds of electro-insulating liquids, so-called dielectric nanofluids. The tendency towards nanofluids research stems from the needs of the power industry’s engineers involved in the design of new insulation systems [13]. Dielectric nanofluids consist of base liquid, which can be mineral oil or esters (synthetic or natural) and nanometric particles (1–100 nm) dissolved or suspended in it. However, nanofluids are more than just the sum of the base components [14]. This means that the produced dielectric nanofluid can have enhanced properties than would be expected, considering its base components.

There are different criteria for the division of nanofillers (nanoparticles). They are most often divided according to the type of material they are made of, and because of their shape or aspect ratio. Considering the first criterion, which is the type of material, nanoparticles are divided into silicon oxides (silica), metal oxides and hydroxides (Al₂O₃, TiO₂, MgO, ZnO, AlO(OH)), nanoclays (montmorillonite) as well as carbon nanotubes and fullerenes (C₆₀ and C₇₀). Taking into account the last criterion, which is the aspect ratio, there are quasi-spherical, cylindrical and plate-shaped nanoparticles [15,16].

Table 1 presents some of dielectric properties of pure electro-insulating liquids and electro-insulating liquids admixed by nanoparticles. The doping of electro-insulating liquids with nanoparticles is aimed at improving such dielectric properties as electrical strength, resistivity, dielectric loss, permittivity [17–27].

| Properties         | MO       | MO + C₆₀   | MO + TiO₂ | NE       | NE + TiO₂ | NE + Fe₃O₄ |
|--------------------|----------|------------|-----------|----------|-----------|------------|
| Breakdown voltage  | 51 [22]  | 53–80 [22] | 81 [26]   | 63 [25]  | 82 [25]   | 60 [27]    |
| [kV]               | 68 [26]  |            |           |          |           |            |
| Resistivity [Ω·m]  | 5.0 × 10¹³ [22] | 4.0 × 10¹³ [22] | 4.7 × 10¹⁴ [23] | 3.5 × 10¹⁴ [23] | 2.1 × 10⁻⁴ [22] | 2.1 × 10⁻⁴ [22] |
| Dielectric loss    | 3.3 × 10⁻⁴ [22,24] | 2.1 × 10⁻⁴ [22,24] | 2.2 [22]  | 2.3 [23] | 2.3 [23]  | 3.9 [26]   |
| Permittivity       | 1.8 × 10⁻⁵ [23] | 1.2 × 10⁻⁵ [23] | 2.2 [22]  | 2.3 [23] | 2.3 [23]  |            |

As shown by Aksamit et al. [22,23] the addition of fullerene C₆₀ to mineral oil caused a several-fold increase in resistivity and a decrease in the dielectric loss by 20–30%. On the other hand, in another publication [24], the same authors reported that the addition of C₆₀ resulted in a decrease in the loss of oil by one to two orders of magnitude. The publication by Zhong et al. [25] presents the results of research showing that the use of titanium oxide TiO₂ nanoparticles in natural ester improved their electrical strength by several dozen percent. In turn, according to Du et al. [26], the use of the same nanoparticles in the case of mineral oil increased its electric strength at alternating voltage by almost 20%, permittivity by over 70% and ignition voltage of partial discharges by almost 10%. Unfortunately, the resistivity has decreased—by almost two orders of magnitude. Fe₃O₄ nanoparticles are also used for the modification of electro-insulating liquids. As Li et al. [27] showed in their research, that the use of Fe₃O₄ nanoparticles in natural ester resulted in an increase of its electrical strength at alternating voltage by 20%, and at surge voltage by 10–30% depending on the polarity. In turn, Fofana shows [28]
that, depending on the type of used nanoparticles, modifying them with electro-insulating liquids can significantly improve the dielectric and thermal properties of nanofluids in relation to the base liquid. As a result, it translates into longer transformer life and better cooling conditions.

In addition to the dielectric properties described above, in electric power equipment, the properties that condition heat transfer are also important. Research is being carried out on the improvement of various liquids (not only electro-insulating) with nanoparticles to improve these properties. Sridhara et al. [29] in their research examined the effect of various nanoparticles, metallic (Cu, Fe) and non-metallic (Al₂O₃, CuO, SiC, SiO₂, TiO₂, Fe₃O₄, C₆₀, AlN), to improve the heat transfer capability of such base liquids as water, mineral oil or ethanol. The type of nanoparticle, its size and shape were analyzed. Attention has been given to properties such as thermal conductivity and viscosity that affect the ability of liquids to exchange heat. Based on their research, Li et al. [27] and Choi et al. [30] found that the addition of Al₂O₃ or AlN nanoparticles improves the thermal conductivity of mineral oil by 8% and the heat transfer coefficient by as much as 20%. The authors of this publication also proved in their research that doping of mineral oil [31] and natural ester [32] with TiO₂ nanoparticles improves selected thermal properties. TiO₂ nanoparticles improve thermal conductivity of mineral oil (about 3–6%) and natural ester (about 1–2%), while C₆₀ nanoparticles improve specific heat of the oil (about 2%) and the ester (about 1–3%).

This article presents the results of research on the thermal properties of synthetic ester modified by titanium oxide TiO₂ and fullerene C₆₀ nanoparticles. The studied nanofluids were characterized by adequate colloidal stability and surface activity. Using the presented nanoparticles and surface modification, the method of obtaining true and colloidal solutions at the concentrations used to improve the dielectric properties of electro-insulating liquids is presented. The obtained nanofluids are characterized by adequate durability of dispersions and thermal properties that are different than those of liquids.

2. Experimental Section

2.1. Used Materials and Their Characteristics

The base liquid used for the research was MIDEL 7131 synthetic ester produced by M&I Materials (Manchester, UK). The used base liquid was characterized by a low level of moisture of 45 ppm and aging, described by the acid number, which value was less than 0.03 mgKOH/g oil. To modify the synthetic ester, commercially available titanium oxide TiO₂ and fullerene C₆₀ nanoparticles were used. The average size of the titanium oxide nanoparticles TiO₂ (Sigma-Aldrich, CAS 13463-67-7, St. Louis, MO, USA) and fullerene C₆₀ (Sigma-Aldrich, CAS 99685-96-8,) was equal 21 nm.

2.2. Preparation of Nanofluids Based on Synthetic Ester and Fullerene C₆₀

Modification of the synthetic ester with fullerene C₆₀ nanoparticles without any additional measures, as in the case of mineral oil [31] and natural ester [32], resulted in the occurrence of the sedimentation process. Therefore, the modified liquid was first mechanically stirred for 2 h. Then, as shown by Peppas et al. [33], the liquid was placed in an ultrasound bath for 5 h at a constant temperature of 60 °C. After that time, it became a true solution. The concentration of fullerene C₆₀ was 0.10 g L⁻¹ and corresponded to the concentration which is used to improve the electro-insulating properties of the synthetic ester by doping with nanoparticles.

2.3. Preparation of Nanofluids Based on Synthetic Ester and TiO₂ Nanoparticles

Similar to the case of nanofluids based on synthetic ester and fullerene C₆₀, modification of the base liquid with titanium oxide TiO₂ nanoparticles without any additional action resulted in the occurrence of the sedimentation process. In addition, after the use of mechanical mixing, heating and sonication, the sedimentation process was still observed. On this basis, it was found that titanium oxide TiO₂ nanoparticles without surface modification do not form a stable dispersion in the synthetic ester.
In order to produce a stable colloidal solution based on synthetic ester and titanium oxide nanoparticles TiO$_2$, as suggested by Chiesa and Das [34], a surface-active substance (dispersant) C$_{18}$H$_{34}$O$_6$ (SPAN 20, Sigma-Aldrich, CAS 1338-39-2), characterized by low molecular weight, was added to the base liquid. This substance allows for the creation of secondary forces (van der Waals, electrostatic, hydrogen bonds) between nanoparticles and modifier [15]. Due to the polar groups that interact with the high energy surface of the nanoparticles, adsorption and accumulation of surfactant molecules at the interface is therefore possible. Thus, the properties of the liquid at the interfaces or surface are changed [35].

In the next step, the base liquid together with the surfactant was subjected to three hours of sonication. Then, dried titanium oxide TiO$_2$ nanoparticles were added to the solution prepared in this way. Uniform dispersion of nanometric particles in a dielectric liquid is crucial because it affects its properties. Due to the fact that nanoparticles, due to high surface energy, very often agglomerate, this can be a big problem [18]. There are many publications that say that clusters of nanoparticles can act as weak points that can become igniting points of destructive processes. As a consequence, it may lead to deterioration of dielectric, mechanical and thermal properties [13,36–39]. Therefore, given the fact that nanoparticles can release their potential when they are evenly dispersed, in order to ensure adequate dispersion and distribution of nanoparticles in the base liquid, the resulting nanofluid has also been subjected to the sonication process. In this case, the duration of sonication was 7 h. After this time, a stable colloidal solution was obtained.

The concentration of surface-active substance in the synthetic ester was 5.00 g·L$^{-1}$. In turn, the concentration of titanium oxide TiO$_2$ equaled 0.82 g·L$^{-1}$. These concentrations correspond to the concentrations that are used in the case of improving the electro-insulating properties of insulating liquids by doping with nanoparticles. It should also be noted that the use of too high concentrations of surface-active substances may result in the deterioration of the properties of base fluids [15].

In order to eliminate the influence of a surface-active substance on the thermal properties of the resulting nanofluids, samples of synthetic ester, modified with a surface-active substance, were also prepared for the tests.

2.4. Measurement of Nano Fluids Thermal Properties

The analyzed properties of the electro-insulating liquids were: thermal conductivity $\lambda$, kinematic viscosity $\nu$, density $\rho$, specific heat $c_p$, and the thermal expansion factor $\beta$- obtained by means of measurements, and the heat transfer factor $\alpha$, which was obtained by means of calculations. The heat transfer factor $\alpha$ was calculated on the basis of equation [4,5]:

$$\alpha = \frac{1}{\sqrt{c \cdot \lambda^{1-n} \cdot \rho^n \cdot \delta^{3n-1} \cdot \beta^n \cdot \rho^n \cdot c_p^n \cdot \nu^{-n} \cdot q^n}},$$

where: $\alpha$- heat transfer factor of the liquid [W·m$^{-2}$·K$^{-1}$], $c$, $\nu$- constants dependent on the flow character, temperature and geometry, $\lambda$- thermal conductivity coefficient [W·m$^{-1}$·K$^{-1}$], $\delta$- gravity [m·s$^{-2}$], $n$, $\rho$- characteristic dimension dependent on the flow character [m], $\beta$- thermal expansion [K$^{-1}$], $\rho$- density [g·l$^{-1}$], $c_p$- specific heat [J·kg$^{-1}$·K$^{-1}$], $\nu$-kinematic viscosity [mm$^2$·s$^{-1}$], $q$- surface thermal load [W·m$^{-2}$]. As it results from the presented equation, if the thermal conductivity, specific heat, density and thermal expansion are higher, the heat transfer coefficient is higher. In turn, the increase in viscosity reduces the heat transfer coefficient.

The above properties are vital in terms of heat transport to the environment by the liquid. The investigations of all the mentioned properties were done for four temperature values: 25, 40, 60, and 80 °C.

A measuring system, designed and built by the authors [40] was used for measuring thermal conductivity of the investigated electro-insulating liquids. Viscosity of the investigated electro-insulating liquids was determined according to standard [41]. Density measurements were done on the basis of standards [42,43]. In turn, specific heat was determined using a differential
scanning calorimeter Mettler Toledo DSC1 (Mettler Toledo, Columbus, OH, USA). To determine the thermal expansion factor, the authors used a measurement system built according to standard [44].

3. Results and Discussion

3.1. Synthetic Ester Modified by Fullerene C\textsubscript{60}

Table 2 presents measurement results of thermal properties and calculation results of the heat transfer factor $\alpha$ of pure synthetic ester and synthetic ester admixed with fullerene C\textsubscript{60}.

Table 2. Measurement results of five thermal properties and calculation results of the heat transfer factor $\alpha$ of pure synthetic ester and synthetic ester admixed by fullerene C\textsubscript{60}, as a function of temperature; SE—synthetic ester.

| Property                                    | Kind of Liquids | SE | SE + C\textsubscript{60} | Temperature |
|---------------------------------------------|-----------------|----|--------------------------|-------------|
| Thermal conductivity $\lambda$ [W m\textsuperscript{-1} K\textsuperscript{-1}] |                 |    |                         | 25°C | 40°C | 60°C | 80°C |
|                                             | SE              | 0.158 | 0.156 | 0.153 | 0.151 |
|                                             | SE + C\textsubscript{60} | 0.159 | 0.157 | 0.153 | 0.151 |
| Kinematic viscosity $\nu$ [mm\textsuperscript{2} s\textsuperscript{-1}] |                 |    |                         | 25°C | 40°C | 60°C | 80°C |
|                                             | SE              | 55.14 | 28.25 | 14.02 | 8.11  |
|                                             | SE + C\textsubscript{60} | 55.51 | 28.47 | 14.35 | 8.27  |
| Specific heat $c_p$ [J kg\textsuperscript{-1} K\textsuperscript{-1}] |                 |    |                         | 25°C | 40°C | 60°C | 80°C |
|                                             | SE              | 1905 | 1964 | 2052 | 2149 |
|                                             | SE + C\textsubscript{60} | 1962 | 2014 | 2094 | 2182 |
| Density $\rho$ [g L\textsuperscript{-1}] |                 |    |                         | 25°C | 40°C | 60°C | 80°C |
|                                             | SE              | 964 | 953 | 940 | 926  |
|                                             | SE + C\textsubscript{60} | 964 | 952 | 940 | 926  |
| Thermal expansion $\beta$ [K\textsuperscript{-1}] |                 |    |                         |       |
|                                             | SE              | 0.00076 | 0.00077 | 0.00078 | 0.00079 |
|                                             | SE + C\textsubscript{60} | 0.00076 | 0.00077 | 0.00078 | 0.00079 |
| Heat transfer factor $\alpha$ [W m\textsuperscript{-2} K\textsuperscript{-1}] |       |    |                         | 25°C | 40°C | 60°C | 80°C |
|                                             | SE              | 83.41 | 98.44 | 116.84 | 134.13 |
|                                             | SE + C\textsubscript{60} | 84.29 | 99.32 | 116.75 | 133.98 |

Thermal conductivity $\lambda$, density $\rho$, and the thermal expansion factor $\beta$ of synthetic ester practically did not change their values as a result of adding fullerenes C\textsubscript{60}. The lack of this influence was noticeable independently of temperature.

In turn, kinematic viscosity $\nu$ increased its value a little as a result of adding C\textsubscript{60} nanoparticles by 0.6\% (for 25 °C), 0.7\% (for 40 °C), 2.3\% (for 60 °C) and by 2.0\% (for 80 °C). As we can observe, this increase was more and more noticeable with temperature increase. Viscosity increase can have a negative influence on the heat transfer factor $\alpha$. Viscosity increase of synthetic ester should be linked with the fact that C\textsubscript{60} nanoparticles are solid material. Adding such material to any liquid will always result in viscosity increase of this liquid.

In contrast, specific heat $c_p$ increased its value as a result of adding fullerenes C\textsubscript{60} by 3.0\% (for 25 °C), 2.6\% (for 40 °C), 2.1\% (for 60 °C) and by 1.5\% (for 80 °C). As we can see, specific heat increase was smaller and smaller with temperature increase. Thus, adding C\textsubscript{60} nanoparticles, can cause an increase of factor $\alpha$ of synthetic ester. Specific heat increase, resulting from adding C\textsubscript{60} nanoparticles to synthetic ester, is caused by the forming of hydrophobic bonds between C\textsubscript{60} and hydrocarbon molecules included in the synthetic ester. Such bonds also explain obtaining a stable true solution after C\textsubscript{60} sonication in the ester. According to the authors of [45], the discussed hydrophobic bonds are very important for particle absorption on the surface of multi-wall carbon nanotubes. These bonds are so strong, that they cause specific heat increase despite a small amount of C\textsubscript{60} (0.01\%) and over two-fold lower values of specific heat for fullerenes [46–48] in reference to non-admixed synthetic ester.

As we can see, adding fullerenes to synthetic ester caused a minimal rise of heat transfer factor $\alpha$ by 1.1\% (for 25 °C) and by 0.9\% (for 40 °C). For a higher temperature (from 60 °C) the heat transfer factor did not change its value. The increase of factor $\alpha$ for lower temperature values was caused by an increase of specific heat $c_p$ by a few percent. This happened despite an increase of viscosity $\nu$ by hardly 1\%. For a higher temperature, factor $\alpha$ practically did not change its value. This resulted from lower increase of specific heat and higher viscosity increase.
3.2. Synthetic Ester Modified by Surface-Active Substance and TiO$_2$ Nanoparticles

3.2.1. Synthetic Ester Modified by Surface-Active Substance

Table 3 presents measurement results of five thermal properties and calculation results of the heat transfer factor $\alpha$ of pure synthetic ester, synthetic ester admixed with a surface-active substance SPAN 20, and synthetic ester admixed with a surface-active substance and TiO$_2$ nanoparticles. The measurements were taken for a wide temperature range from 25 °C to 80 °C.

**Table 3.** Measurement results of five thermal properties and calculation results of the heat transfer factor $\alpha$ of pure synthetic ester, synthetic ester admixed by a surface-active substance SPAN 20, and synthetic ester admixed by surface-active substance and TiO$_2$ nanoparticles, as a function of temperature.

| Property Kind of Liquids | Temperature |
|-------------------------|-------------|
|                         | 25 °C       | 40 °C       | 60 °C       | 80 °C       |
| Thermal conductivity $\lambda$ [W m$^{-1}$ K$^{-1}$] | SE | 0.158 | 0.156 | 0.153 | 0.151 |
|                         | SE + SPAN 20 | 0.158 | 0.156 | 0.153 | 0.152 |
|                         | SE + SPAN 20 + TiO$_2$ | 0.163 | 0.160 | 0.157 | 0.154 |
| Kinematic viscosity $\nu$ [mm$^2$ s$^{-1}$] | SE | 55.14 | 28.25 | 14.02 | 8.11 |
|                         | SE + SPAN 20 | 55.72 | 28.63 | 14.67 | 8.31 |
|                         | SE + SPAN 20 + TiO$_2$ | 55.91 | 28.97 | 14.86 | 8.37 |
| Specific heat $c_p$ [J kg$^{-1}$ K$^{-1}$] | SE | 1905 | 1994 | 2105 | 2149 |
|                         | SE + SPAN 20 | 1937 | 2082 | 2176 |
|                         | SE + SPAN 20 + TiO$_2$ | 1976 | 2115 | 2207 |
| Density $\rho$ [g L$^{-1}$] | SE | 964 | 954 | 941 | 926 |
|                         | SE + SPAN 20 | 964 | 954 | 941 |
|                         | SE + SPAN 20 + TiO$_2$ | 965 | 954 | 941 |
| Thermal expansion $\beta$ [K$^{-1}$] | SE | 0.00076 | 0.00077 | 0.00078 | 0.00079 |
|                         | SE + SPAN 20 | 0.00076 | 0.00078 | 0.00078 | 0.00079 |
|                         | SE + SPAN 20 + TiO$_2$ | 0.00075 | 0.00076 | 0.00078 | 0.00079 |
| Heat transfer factor $\alpha$ [W m$^{-2}$ K$^{-1}$] | SE | 83.41 | 98.44 | 116.84 | 134.13 |
|                         | SE + SPAN 20 | 83.54 | 98.78 | 115.98 | 134.39 |
|                         | SE + SPAN 20 + TiO$_2$ | 85.61 | 100.24 | 118.33 | 135.95 |

The measurements were taken for a wide temperature range from 25 °C to 80 °C. Lack of change of thermal properties was visible for the whole temperature range, within which the investigations were done.

Adding SPAN 20 disperser caused an increase of kinematic viscosity $\nu$ by 1.1% (for 25 °C), 1.4% (for 40 °C), 4.6% (for 60 °C), and 2.5% (for 80 °C). As we can see, this increase was greater with temperature rise. This increase was caused by higher viscosity of the disperser in comparison to synthetic ester viscosity.

The surface-active substance SPAN 20 resulted in an increase of specific heat $c_p$ by 1.7% (for 25 °C), 1.5% (for 40 °C), 1.5% (for 60 °C), and 1.3% (for 80 °C). This is probably due to the making hydrogens bonds between the oxygen of the ester group of synthetic ester and SPAN 20 disperser’s (C$_{18}$H$_{34}$O$_6$) hydroxylic groups. Therefore, a larger amount of energy (heat) is required to warm up the investigated system. The substances, that are characterized by the presence of hydrogen bonds, have a large thermal capacity. The higher the substance’s thermal capacity is, the larger is its specific heat. This increase was lower with temperature increase.

As we can observe, adding the disperser caused very little changes of heat transfer factor $\alpha$, which do not exceed 1%. This means that the disperser neither improved nor deteriorated the ability of synthetic ester to transport heat.

3.2.2. Synthetic Ester Modified by Surface-Active Substance and TiO$_2$ Nanoparticles

Thermal conductivity $\lambda$ of synthetic ester increased as a result of adding TiO$_2$ nanoparticles and SPAN 20 disperser by 3.2% (for 25 °C), 2.6% (for 40 °C), 2.6% (for 60 °C), and 2.0% (for 80 °C). As we
can see, this increase was smaller and smaller with temperature increase. This increase is due to titanium oxide nanoparticles, because adding only the disperser did not cause changes of thermal conductivity. Thermal conductivity increases results from much higher thermal conductivity of TiO$_2$ nanoparticles (about 22 W·m$^{-1}$·K$^{-1}$) in comparison to the thermal conductivity of the ester itself (about 0.15 W·m$^{-1}$·K$^{-1}$).

We can state on the basis of the obtained results that kinematic viscosity $\nu$ of synthetic ester admixed with TiO$_2$ nanoparticles and SPAN 20 disperser increased by 1.4% (for 25°C), 2.6% (for 40°C), 6.0% (for 60°C), and 3.2% (for 80°C). It is caused by both SPAN 20 disperser and TiO$_2$ nanoparticles. Viscosity increase should be linked with much higher viscosity of the added disperser and adding solid materials (titanium oxide), the adding of which to liquid always results in viscosity increase.

Viscosity increase should be linked with much higher viscosity of the added disperser and adding solid materials (titanium oxide), the adding of which to liquid always results in viscosity increase. We can conclude on the basis of the measurement results that specific heat $c_p$ of the synthetic ester admixed with SPAN 20 disperser and TiO$_2$ nanoparticles, increased by 3.7% (for 25°C), 3.4% (for 40°C), 3.1% (for 60°C), and 2.7% (for 80°C). This increase is lower and lower with temperature increase. This increase results probably from making hydrogen bonds between the oxygen coming from a TiO$_2$ particle, the oxygen of the ester group of synthetic ester and SPAN 20 disperser’s hydroxylic groups. Because of making hydrogen bonds, a larger amount of energy (heat) is required to warm up the investigated system. The substances in which there are hydrogen bonds are characteristic of large thermal capacity (e.g., water). In the case of the investigated nanofluid, hydrogen bonds increase its thermal capacity. Thermal capacity shows how much energy the particles are able to store. The more energy a particle can receive (the more freedom degrees) the higher is its thermal capacity. In turn, if the substance’s thermal capacity is higher, its specific heat is higher. Hydrogen bonds also allow storing additional energy. Thus, as a result of making hydrogen bonds, more heat was necessary to warm up a sample in the created nanofluid, because additional energy was demanded, required to break hydrogen bonds. Because heat is supplied to the substance, a part of this energy is used for breaking hydrogen bonds, not for raising its temperature. In the case of the nanofluid made on the base of mineral oil, surface-active substance SPAN 20 and TiO$_2$ nanoparticles, there is no possibility to make hydrogen bonds with oil particles.

Density $\rho$ and the thermal expansion factor $\beta$ of synthetic ester practically did not change their values as a result of adding TiO$_2$ nanoparticles and SPAN 20 surface-active substance. This means that titanium oxide TiO$_2$ did not have any influence on these thermal properties, because SPAN 20 disperser did not have such influence either. Lack of change in the thermal properties referred to the whole temperature range, for which the research was done.

As shown in Table 3, adding titanium oxide and disperser caused an increase of heat transfer factor $\alpha$ by 2.6% (for 25°C), 1.8% (for 40°C), 1.3% (for 60°C), and 1.4% (for 80°C). As we can see, this increase diminishes a little with temperature rise. This increase was mainly affected by increase of thermal conductivity $\lambda$ and increase of specific heat $c_p$, despite increase of kinematic viscosity $\nu$. This means that adding titanium oxide (with the surface-active substance) to synthetic ester to improve electric properties of ester has a positive effect on their ability to heat transfer.

Some calculation of temperature distribution in transformer was made in order to indicate the impact of TiO$_2$ nanoparticles on cooling system efficiency. The calculations were based on the following formula:

$$\Delta T = \frac{q}{\alpha}$$  \hspace{1cm} (2)

where: $\Delta T$—temperature decrease in liquid (between transformer windings and a tank) [°C], $q$- surface heat load on the windings (there was chosen 3000 W·m$^{-2}$, because it is typical surface heat load on transformer windings surface). Results of calculations are presented in Table 4.
Table 4. Impact of TiO₂ nanoparticles (with SPAN 20) on temperature distribution in synthetic ester.

| Kind of Liquid | Heat Transfer Coefficient \( \alpha \) [W m\(^{-2}\) K\(^{-1}\)] for 25 °C | Surface Heat Load \( q \) [W m\(^{-2}\)] | Temperature Decrease in Liquid \( \Delta T \) [°C] |
|----------------|-------------------------------------------------|------------------|-----------------|
| Pure synthetic ester | 83.41 | 3000 | 35.97 |
| SE + SPAN 20 + TiO₂ | 85.61 | 3000 | 35.04 |
| Difference of \( \Delta T \) between pure and admixed liquid [°C] | | | 0.93 |

| Heat transfer coefficient \( \alpha \) [W m\(^{-2}\) K\(^{-1}\)] for 40 °C | Surface Heat Load \( q \) [W m\(^{-2}\)] | Temperature decrease in liquid \( \Delta T \) [°C] |
|-------------------------------------------------|------------------|-----------------|
| Pure synthetic ester | 98.44 | 3000 | 30.48 |
| SE + SPAN 20 + TiO₂ | 100.24 | 3000 | 29.93 |
| Difference of \( \Delta T \) between pure and admixed liquid [°C] | | | 0.55 |

| Heat transfer coefficient \( \alpha \) [W m\(^{-2}\) K\(^{-1}\)] for 60 °C | Surface Heat Load \( q \) [W m\(^{-2}\)] | Temperature decrease in liquid \( \Delta T \) [°C] |
|-------------------------------------------------|------------------|-----------------|
| Pure synthetic ester | 116.84 | 3000 | 25.68 |
| SE + SPAN 20 + TiO₂ | 118.33 | 3000 | 25.35 |
| Difference of \( \Delta T \) between pure and admixed liquid [°C] | | | 0.33 |

| Heat transfer coefficient \( \alpha \) [W m\(^{-2}\) K\(^{-1}\)] for 80 °C | Surface Heat Load \( q \) [W m\(^{-2}\)] | Temperature decrease in liquid \( \Delta T \) [°C] |
|-------------------------------------------------|------------------|-----------------|
| Pure synthetic ester | 134.13 | 3000 | 22.37 |
| SE + SPAN 20 + TiO₂ | 135.95 | 3000 | 22.07 |
| Difference of \( \Delta T \) between pure and admixed liquid [°C] | | | 0.30 |

On the basis of Table 4, it is possible to say, that nanoparticles TiO₂ (and SPAN 20) have some small positive impact on heat transfer factor \( \alpha \) of liquid, that means, also on the cooling system in the transformer. The temperature in the hot spot of the transformer filled by nanofluid will be smaller compared to the hot spot in the transformer filled by pure synthetic ester. The impact is very small, and it decreases with temperature increase: the impact was 0.93 °C for 25 °C, and only 0.30 °C for 80 °C. Even if the impact is very small, it plays some positive role in the aging process of the transformer (particularly for the transformer insulation system). According to Montsinger law, known as the “8 degrees law”, reducing the transformer temperature by about 8 °C almost doubles the lifespan of the transformer.

4. Conclusions

Adding C\(_{60}\) nanoparticles to synthetic ester did not practically change the value of the heat transfer factor \( \alpha \) of the ester. Moreover, for the temperature of the range 25–40 °C, the value of factor \( \alpha \) rose slightly (by about 1%). Lack of noticeable changes of factor \( \alpha \) is caused by a compensating action of thermal conductivity and specific heat of the ester on the one hand, and ester viscosity on the other. The authors obtained similar results in the case of C\(_{60}\) nanoparticles added to such electro-insulating liquids as mineral oil and natural ester. In the case of these two liquids, the heat transfer coefficient \( \alpha \) also increased by about 1% [31,32].

Adding SPAN 20 surface-active substance to the synthetic ester did not affect the heat transfer factor. This result was influenced by viscosity increase (causing a drop of factor \( \alpha \)) and specific heat increase (causing a rise of factor \( \alpha \)). On this basis, we can state that disperser added to synthetic ester in order to prepare a stable colloidal solution with nanoparticles does not affect the ability of ester to transfer heat. The authors obtained similar results for the SPAN 20 surfactant added to other electro-insulating liquids such as mineral oil and natural ester. The coefficient of heat transfer \( \alpha \) did not also change its value [31,32].

Adding titanium oxide TiO₂ nanoparticles (with SPAN 20 disperser) to synthetic ester resulted in an increase of factor \( \alpha \). This increase is caused mainly by an increase of thermal conductivity and specific heat as a result of presence of titanium oxide nanoparticles. The authors obtained similar
results in the case of TiO$_2$ and SPAN nanoparticles added to mineral oil and natural ester. The heat transfer coefficient $\alpha$ also increased by about 1–3% [31,32].

Summing up, we can say that adding fullerene nanoparticles to synthetic ester did not cause any considerable changes of the heat transfer factor $\alpha$. It means that application of synthetic ester admixed with nanoparticles C$_{60}$, in order to improve dielectric properties, does not change transfer of heat in power transformer.

In contrast, adding titanium oxide TiO$_2$ nanoparticles (with SPAN 20 disperser) resulted in a positive increase of factor $\alpha$. On this basis, we can state that the use of synthetic ester admixed with nanoparticles TiO$_2$, in order to make dielectric properties better, improves transfer of heat in the transformer.

**Author Contributions:** Section 1 was prepared by Z.N. The nanofluids described in Section 2 were prepared by G.D., and Section 2 was prepared by G.D. All the authors jointly planned the experiment, described by G.D., in Section 3. Thermal properties of the obtained nanofluids were measured by G.D. The heat transfer factor was calculated by Z.N. The experiment was conducted by Z.N. and G.D. Conclusions were prepared jointly by all the authors.

**Funding:** The research was financed from resources of the Ministry of Science and Higher Education for Statutory Activities No. 04/41/DS-PB/4293, name of the task: The influence of various parameters on thermal properties of dielectric liquids used in the high voltage transformer.

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

**References**

1. Gong, R.H.; Ruan, J.J.; Chen, J.Z.; Quan, Y.; Wang, J.; Duan, C.H. Analysis and experiment of hot-spot temperature rise of 110 kV three-phase three-limb transformer. *Energies* **2017**, *10*, 1079. [CrossRef]

2. Roslan, M.H.; Azis, N.; Ab Kadir, M.Z.A.; Jasni, J.; Ibrahim, Z.; Ahmad, A. A simplified top-oil temperature model for transformers based on the pathway of energy transfer concept and the thermal-electrical analogy. *Energies* **2017**, *10*, 1843. [CrossRef]

3. Lopatkiewicz, R.; Nadolny, Z.; Przybylek, P. The influence of chosen parameters on thermal conductivity of winding insulation describing temperature distribution in transformer. *Prz. Elektrotech.* **2012**, *88*, 126–129. (In Polish)

4. Dombek, G.; Nadolny, Z. Liquid kind, temperature, moisture, and ageing as an operating parameters conditioning reliability of transformer cooling system. *Eksplot. Niezawodn.* **2016**, *18*, 413–417. [CrossRef]

5. Dombek, G.; Nadolny, Z. Thermal properties of mixture of synthetic and natural esters in terms of their applications in high voltage power transformers. *Eksplot. Niezawodn.* **2017**, *19*, 62–67. [CrossRef]

6. Rozga, P. Streamer propagation and breakdown in a very small point-insulating plate gap in mineral oil and ester liquids at positive lightning impulse voltage. *Energies* **2016**, *9*, 467. [CrossRef]

7. Experiences in Service with New Insulating Liquids; Cigré Technical Brochure 436; International Council on Large Electric Systems (CIGRE): Paris, France, 2010.

8. Malinowski, G.; Moranda, H.; Siodla, K. Dependence of creeping partial discharge activity in a synthetic esters-paper insulating system on the temperature. In Proceedings of the IEEE International Conference on High Voltage Engineering and Application (ICHVE), Poznan, Poland, 8–11 September 2014; pp. 1–3.

9. Rozga, P.; Stanek, M.; Pasternak, B. Characteristics of negative streamer development in ester liquids and mineral oil in a point-to-sphere electrode system with a pressboard barrier. *Energies* **2018**, *11*, 1088. [CrossRef]

10. Lewand, L. *Understanding Water in Transformer System*; Neta Word Report; Spring: Washington, DC, USA, 2002; pp. 1–4.

11. Lv, Y.; Rafiq, M.; Li, C.; Shan, B. Study of dielectric breakdown performance of transformer oil based magnetic nanofluids. *Energies* **2017**, *10*, 1025. [CrossRef]

12. Dombek, G.; Gielniak, J.; Wroblewski, R. Fire safety and electrical properties of mineral oil/synthetic ester mixtures. In Proceedings of the IEEE International Symposium on Electrical Insulating Materials (ISEIM), Toyohashi, Japan, 11–15 September 2017; pp. 227–230.

13. Lau, K.Y.; Vaughan, A.S.; Chen, G. Nanodielectrics: Opportunities and challenges. *IEEE Electr. Insul. Mag.* **2015**, *31*, 45–54. [CrossRef]
14. Nelson, J.K. Dielectric Polymer Nanocomposites; Springer: New York, NY, USA, 2010; pp. 31–64, ISBN 978-1-4419-1591-7.

15. Andritsch, T.; Fabiani, D.; Vazquez, I.R. Nanodielectrics—Examples of preparation and microstructure. IEEE Electr. Insul. Mag. 2013, 29, 21–28. [CrossRef]

16. Castellon, J.; Vazquez, I.R.; Frechette, M. Nanocomposite characterization and diagnostic tools. IEEE Electr. Insul. Mag. 2013, 29, 37–48. [CrossRef]

17. Aksamit, P.; Zmarzly, D.; Boczar, T. Electrostatic properties of aged fullerene-doped mineral oil. IEEE Trans. Dielectr. Electr. Insul. 2011, 18, 1459–1462. [CrossRef]

18. Cherney, E.A. Nanodielectrics applications—today and tomorrow. IEEE Electr. Insul. Mag. 2013, 29, 59–65. [CrossRef]

19. Saidur, R.; Leong, K.Y.; Mohammad, H.A. A review on applications and challenges of nanofluids. Renew. Sustain. Energy Rev. 2011, 15, 1646–1668. [CrossRef]

20. Segal, V.; Hjortsberg, A.; Rabinovich, A.; Nattrass, D.; Raj, K. AC (60 Hz) and impulse breakdown strength of a colloidal fluid based on transformer oil and magnetite nanoparticles. In Proceedings of the IEEE International Symposium on Electrical Insulation, Arlington, VA, USA, 7–10 June 1998; pp. 619–622.

21. Sartoratto, P.P.C.; Neto, A.V.S.; Lima, E.C.D. Preparation and electrical properties of oil-based magnetic fluids. J. Appl. Phys. 2005, 97, 10Q917. [CrossRef]

22. Aksamit, P.; Zmarzly, D. Dielectric properties of fullerene-doped insulation liquids. In Proceedings of the IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Virginia Beach, VA, USA, 18–21 October 2009; pp. 212–215.

23. Aksamit, P.; Zmarzly, D.; Boczar, T.; Szmechta, M. Aging properties of fullerene doped transformer oils. In Proceedings of the IEEE International Symposium on Electrical Insulation (ISEI), San Diego, CA, USA, 6–9 June 2010; pp. 1–4.

24. Boczar, T.; Zmarzly, D.; Aksamit, P.; Lorenz, M. Electrostatic properties of fullerene-doped hydrocarbons. In Proceedings of the IEEE International Symposium on Electrical Insulating Materials (ISEIM), Mie, Japan, 7–11 September 2008; pp. 295–298.

25. Zhong, Y.; Lv, Y.; Li, C. Insulating properties and charge characteristics of natural ester fluid modified by TiO$_2$ semiconductive nanoparticles. IEEE Trans. Dielectr. Electr. Insul. 2013, 20, 135–140. [CrossRef]

26. Du, Y.; Lv, Y.; Li, C.; Chen, M.; Zhong, Y.; Zhou, J.; Li, X.; Zhou, Y. Effect of semiconductive nanoparticles on insulating performances of transformer oil. IEEE Trans. Dielectr. Electr. Insul. 2012, 19, 770–776. [CrossRef]

27. Li, J.; Zhang, Z.; Zou, P.; Grzybowski, S.; Zahn, M. Preparation of a vegetable oil-based nanofluids and investigation of its breakdown and dielectric properties. IEEE Electr. Insul. Mag. 2012, 28, 43–50. [CrossRef]

28. Fofana, I. 50 years in the development of insulating liquids. IEEE Electr. Insul. Mag. 2013, 29, 13–25. [CrossRef]

29. Sridhara, V.; Gowrishankar, B.S.; Satapathy, L.N. Nanofluids—A new promising fluid for cooling. Trans. Indian Ceram. Soc. 2009, 68, 1–17. [CrossRef]

30. Choi, C.; Yoo, H.S.; Oh, J.M. Preparation and heat transfer properties of nanoparticle-in-transformer oil dispersions as advanced energy-efficient coolants. Curr. Appl. Phys. 2008, 6, 710–712. [CrossRef]

31. Nadolny, Z.; Dombek, G.; Przybyłek, P.; Przadka, D. Thermal properties of mineral oil admixed with C$_{60}$ and TiO$_2$ nanoparticles. In Proceedings of the IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Toronto, ON, Canada, 16–19 October 2016; pp. 538–541.

32. Dombeł, G.; Nadolny, Z.; Przybyłek, P. Cooling properties of natural ester modified by nanopowders fullerene C$_{60}$ and TiO$_2$ for high voltage insulation applications. In Proceedings of the IEEE International Symposium on Electrical Insulating Materials (ISEIM), Toyohashi, Japan, 11–15 September 2017; pp. 442–445.

33. Peppas, G.D.; Bakandrisos, A.; Charalampakos, V.P.; Pyrgioti, E.C.; Tucek, J.; Zboril, R.; Gonos, I.F. Ultrastable natural ester-based nanofluids for high voltage insulation applications. ACS Appl. Mater. Interface 2016, 8, 25202–25209. [CrossRef] [PubMed]

34. Chiesa, M.; Das, S.K. Experimental investigation of the dielectric and cooling performance of colloidal suspensions in insulating media. Colloids Surf. A 2009, 335, 88–97. [CrossRef]

35. Rosen, M.J.; Kunjappu, J.T. Surfactants and Interfacial Phenomena, 4th ed.; Wiley: Hoboken, NJ, USA, 2012; pp. 235–271. ISBN 978-0-470-54194-4.

36. Vaughan, A.S.; Swingler, S.G.; Zhang, Y. Polyethylene nanodielectrics: The influence of nanoclays on structure formation and dielectric breakdown. IEEE Trans. Fund. Mater. 2006, 126, 1057–1063. [CrossRef]
37. Wernik, J.M.; Meguid, S.A. On the mechanical characterization of carbon nanotube reinforced epoxy adhesives. *Mater. Des.* **2014**, *59*, 19–32. [CrossRef]
38. Ali, A.D.; Shimpi, N.G.; Mishra, S. Thermal, mechanical and morphological properties of surface-modified montmorillonite-reinforced viton rubber nanocomposites. *Polym. Int.* **2014**, *63*, 338–346. [CrossRef]
39. Parameshwaran, R.; Kalaiselvam, M. Effect of aggregation on thermal conductivity and heat transfer in hybrid nanocomposite phase change colloidal suspensions. *Appl. Phys. Lett.* **2013**, *103*, 193113. [CrossRef]
40. Dombek, G.; Nadohny, Z.; Przybylek, P. Investigation of parameters which have the influence on the ability of heat transport of electro-insulating liquids. *Prz. Elektrotech.* **2014**, *10*, 148–151. (In Polish)
41. International Organization of Standardization (ISO). ISO 3104:1994: Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity; International Organization of Standardization (ISO): Geneva, Switzerland, 1994.
42. International Organization of Standardization (ISO). ISO 3675:1998: Crude Petroleum and Liquid Petroleum Products—Laboratory Determination of Density—Hydrometer Method; International Organization of Standardization (ISO): Geneva, Switzerland, 1998.
43. International Organization of Standardization (ISO). ISO 649-1:1981: Laboratory Glassware—Density Hydrometers for General Purposes—Part 1: Specification; International Organization of Standardization (ISO): Geneva, Switzerland, 1981.
44. American Society for Testing and Materials (ASTM). ASTM D 1903-96: Standard Test Method for Coefficient of Thermal Expansion of Electrical Insulating Liquids of Petroleum Origin, and Askarels; American Society for Testing and Materials (ASTM): West Conshohocken, PA, USA, 1996.
45. Kragulj, M.; Trickovic, J.; Dalmacija, B.; Kukovecz, A.; Konya, Z.; Molnar, J.; Roncevic, S. Molecular interactions between organic compounds and functionally modified multiwalled carbon nanotubes. *Chem. Eng. J.* **2013**, *225*, 144–152. [CrossRef]
46. Allen, K.; Hellman, F. Specific heat of endohedral and higher fullerene thin films. *J. Chem. Phys.* **1999**, *111*, 5291–5294. [CrossRef]
47. Olson, J.R.; Topp, K.A.; Pohl, R.O. Specific-heat and thermal-conductivity of solid fullerenes. *Science* **1993**, *259*, 1145–1148. [CrossRef] [PubMed]
48. Tewari, S.P.; Silotia, P.; Bera, K. Effect of cubic and planar collective and localized modes on the specific heat of C60 fullerite for 0.2 ≤ T ≤ 300 K. *Solid State Commun.* **1998**, *107*, 129–133. [CrossRef]