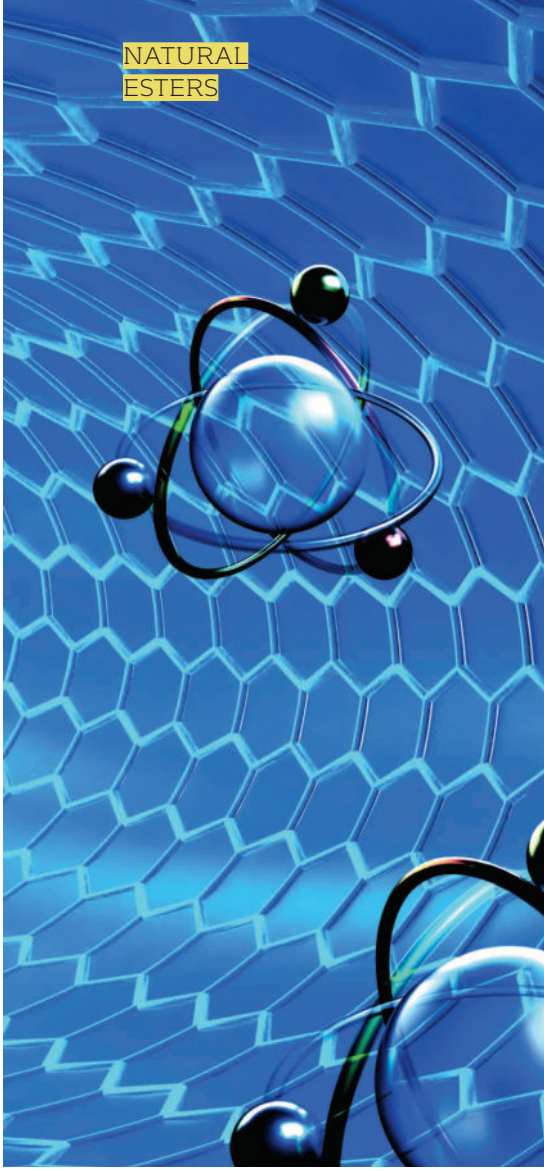


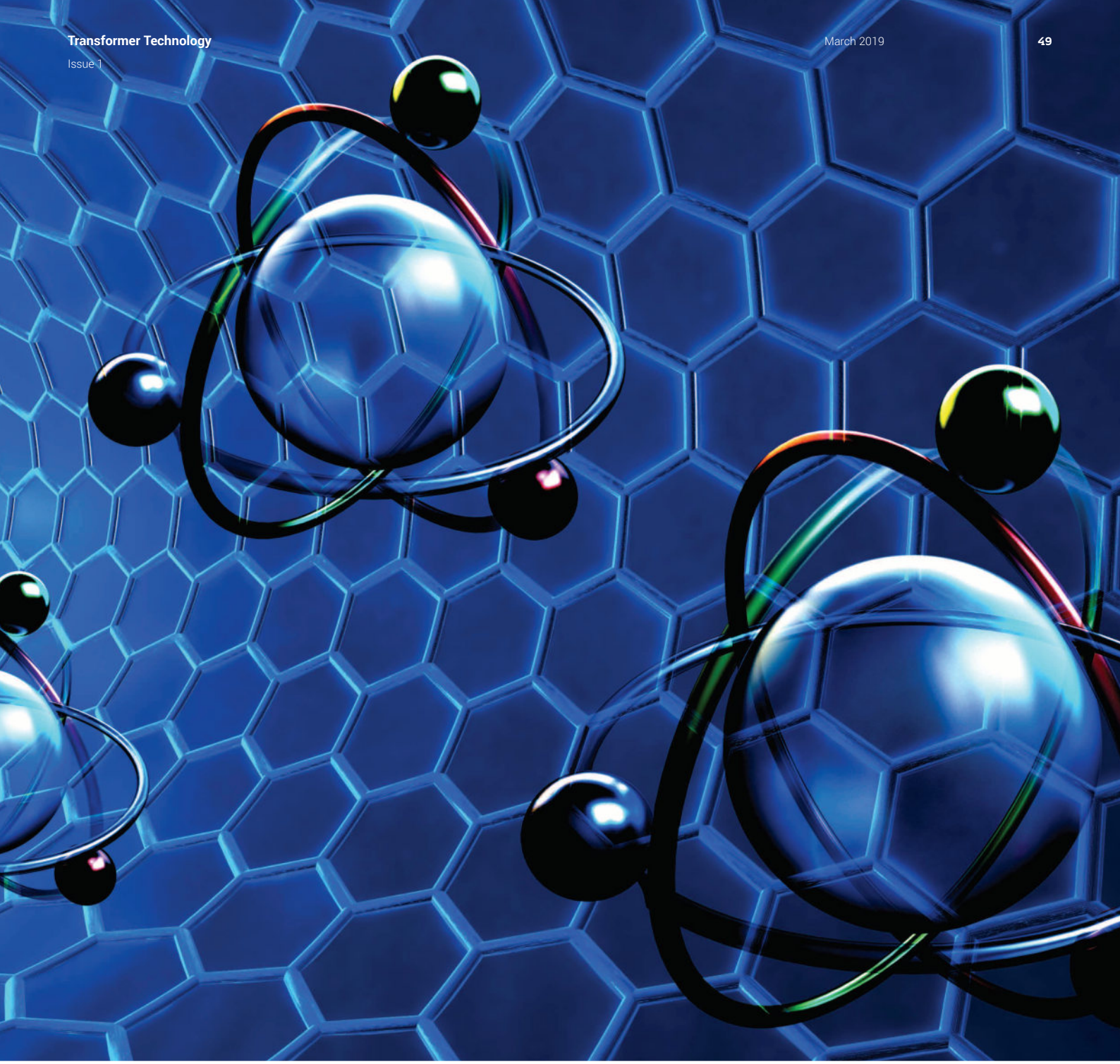
New Developments in Natural Ester Fluids:

Modification by Addition of Nanoparticles Applied in Electrical Transformers

by **Corné Dames**

The main advantage of natural esters is the possibility of using domestic raw materials with a relatively low price and suitable properties, which include biodegradability.

Corné Dames is the Managing Director of Independent Transformer Consultants, always striving to keep on top of new developments and research. She has expertise as Laboratory Manager in the analysis of transformer oils and as diagnostician identifying problem areas in transformers, as well as profiling of transformers according to available results thus empowering the customer to take preventative steps in maintenance. Corné has vast practical and theoretical knowledge on reliability maintenance programs. Coming from a strong chemical background she has insight in all the chemical processes that is part of the transformer system coupled with technical insight helps customers optimise their reliability maintenance and electrical asset lifetime.



New insulating liquid materials development is guided by multiple factors such as environmental requirements and other safety and economic considerations. Therefore, transformer manufacturers have to consider new specifications related to these new requirements.

The vegetable-oil based transformer fluids are increasingly replacing mineral oil-based products in the marketplace. These oils are successful because they perform better in various aspects than mineral oil products and they provide definite environmental and safety gains.

However, some modifications to natural esters are needed to make them more competitive as an insulating fluid. By filtration, nanoparticles addition and oxidation stabilisers added, these natural ester fluids display the necessary characteristics to compete with mineral oils as a replacement for dielectric fluid as part of the transformer insulating systems.

Advantages of Natural Esters

By adding nanoparticles to the natural ester fluids there should be an improvement to the key electrical properties of the fluid.

There are a significant number of advantages that natural esters have as dielectric fluid in transformers:

- Better environmental and health profile than conventional mineral oil
- High bio-degradability, thus leading to easier oil spill management solutions
- Higher flash and fire points that assist in overall safety which can result in lower substation upgrade costs.
- Interactions between the fluid and cellulose have been identified to extend insulation life
- 95% bio-based, providing a very high degree of sustainability
- A unique ability to absorb moisture contained in aging paper that can extend insulation life by a factor of as much as five
- Helping, chemically, to prevent long cellulose paper molecules from scission (i.e. aging) when exposed to heat
- Increased overloading capability and longer transformer insulation life
- Lower lifecycle costs and better utilization of assets
- Coming from renewable resources makes them recyclable and reusable
- Lower gassing tendency under electrical stresses and better resistance to sludge formation
- Due to their viscosity and ability to polymerise when thin layers are exposed to warmth and air flow, they do not spread along the surface and into subsurface soil in the case of spillage

In general, vegetable oil is fully miscible with traditionally used mineral oils, so it can be used to refill existing transformers. Additionally, corrosive sulphur is not present in natural esters. Considering their fire point is much higher than that of mineral oil, natural esters are a **much safer choice for areas where a) there is a risk of human life, b) there are high down time costs, c) there is difficult evacuation of surrounding areas, and d) where transformer replacement time and cost are posing a problem**.

Esters have a lower calorific value than mineral oil, providing less energy units per weight than mineral oil in the event of a fire. The by-products of ester fluid combustion are water, carbon monoxide and carbon dioxide which are less toxic than the carbon, nitrogen and sulphur oxides produced by mineral oil fire.

Disadvantages of Natural Esters

While the list of advantages above is significant, there are some disadvantages to the use of natural esters. Oxidation stability is the greatest concern. The natural ester is the most susceptible to oxidation, more so than all the available oils. Therefor **the exposure to oxygen and moisture should be kept at a minimum**.
The following characteristics are preventing natural esters from being deployed as an entirely technically acceptable replacement for mineral oils:

- Higher viscosity
- High pour point
- Higher permittivity
- Low oxidation stability
- No legislative path and test methods
- Durability problems in short high voltage impulse resistance

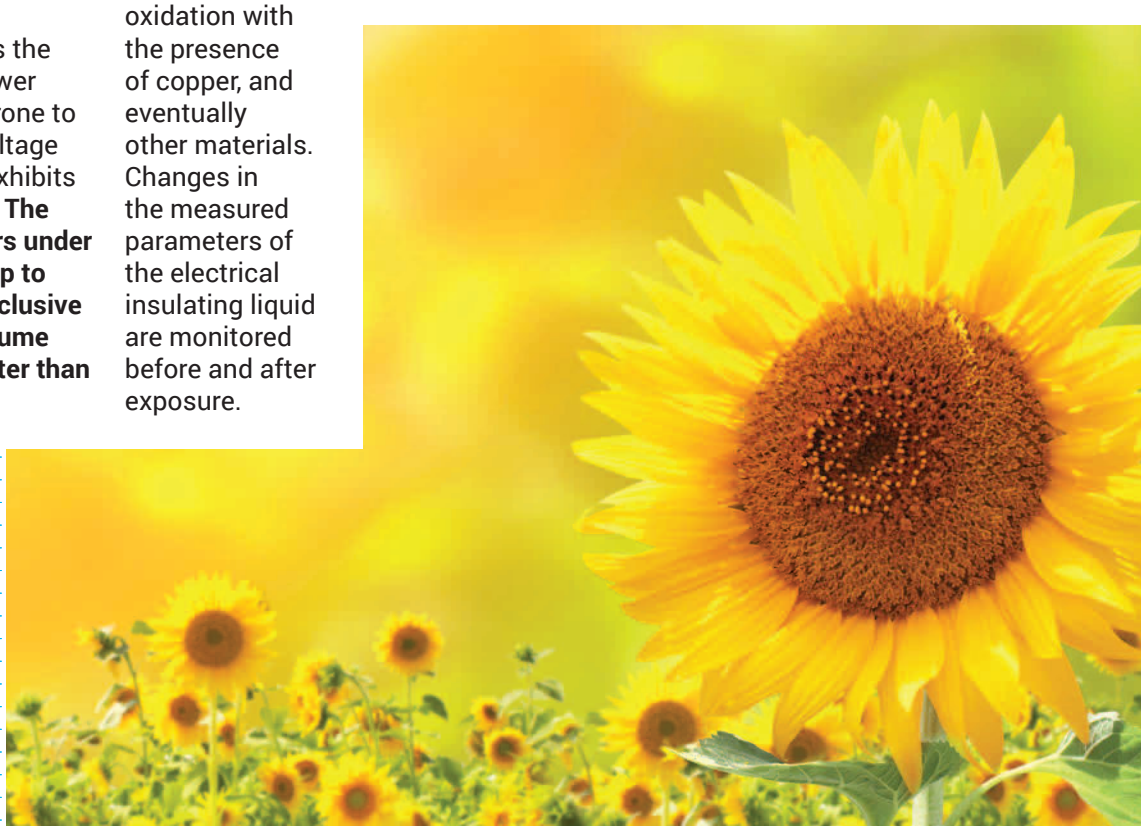
Assessment of Natural Esters for Further Development of Their Electrical Properties

Two types of natural esters have been identified for industrial application – rapeseed (Brassica napus) and sunflower (Helianthus Annuus) oil. However, the high number of poly and mono unsaturated fatty acids keeps the oil in a liquid state, even in lower temperatures, but makes it prone to oxidation. When AC stress voltage is applied, the sunflower oil exhibits a higher rate of deterioration. **The behavior of both natural esters under elevated temperature (25°C up to 140°C) is similar, with no conclusive differences. The value for volume resistivity for rapeseed is better than that of sunflower oil.**

There is no fully implemented legislative guidelines for the use of natural esters in transformers so far, but some properties are given in IEC 62770:2013 - "Fluids for Electrotechnical Applications – Unused Natural Esters for Transformers and Similar Electrical Equipment" [1]. The values for the individual parameters are mentioned in the middle column of Tables 4 and 5 in [1].

It is obvious that these oils could not fully comply with the requirements of Standard IEC 62770 [1] without modifications. These oils could not meet the values for some key parameters e.g. Breakdown Voltage (BDV), Acid number, water content and dissipation factor tan δ. Therefore, adjusting the insulating liquid for the desired purpose was needed. The vegetable oil needed to be passed through a column filled with a suitable sorbent and the addition of an oxidation inhibitor at the corresponding concentration. The modified rapeseed passed the test of oxidative stability (TOS) according to method C in standard IEC 61125 [2]. The TOS is based on the exposure of an oil sample by oxidation with the presence of copper, and eventually other materials. Changes in the measured parameters of the electrical insulating liquid are monitored before and after exposure.

Titanium Dioxide with a silica surface treatment (SFT TiO_2) has the maximum positive effect on breakdown voltage.



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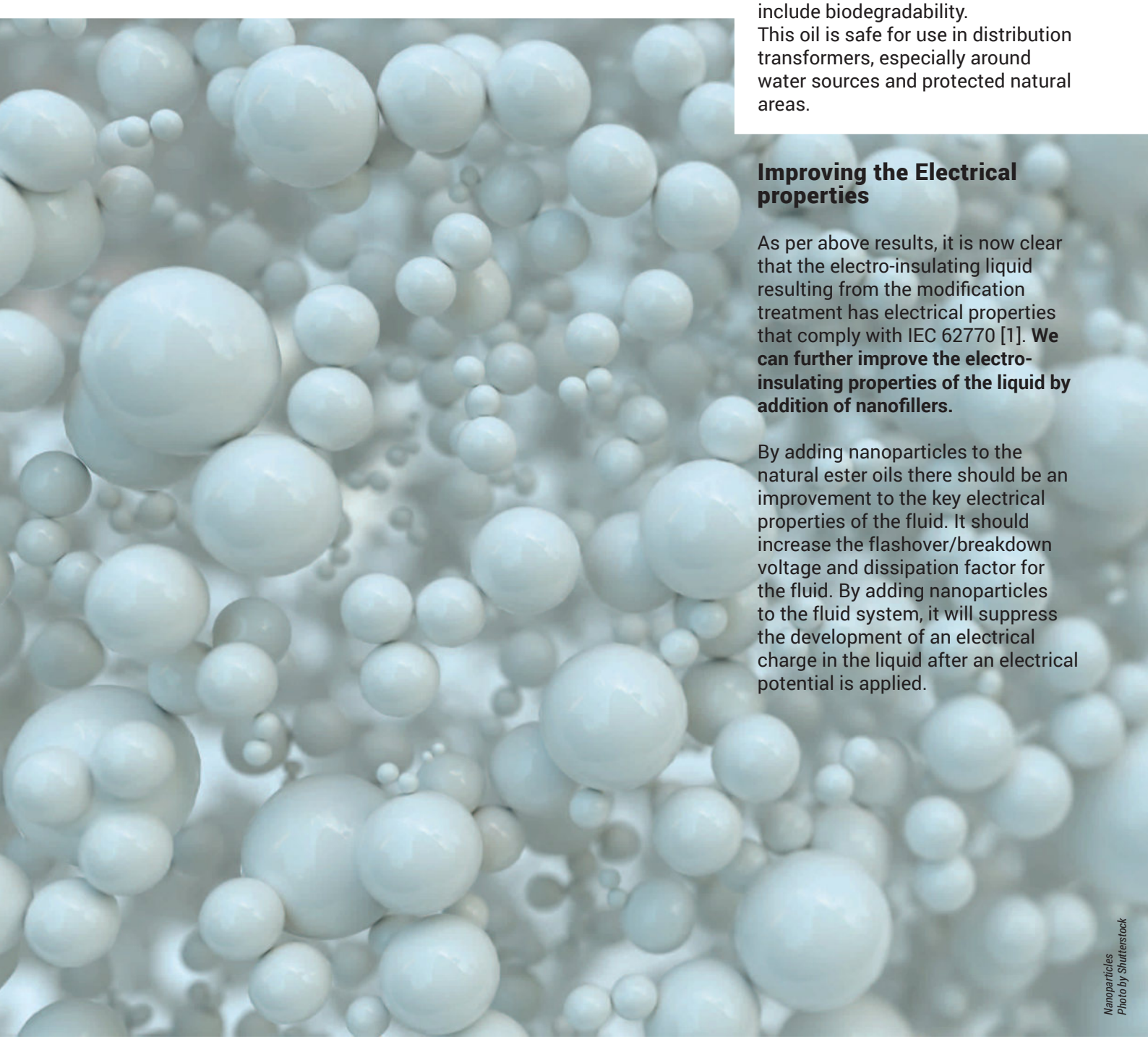
Preparation of Electro-insulating Ester Fluid

By filtering the oil for a 24-hour cycle through a composite pulp filter the acid number comes down to acceptable values. Furthermore, an oxidation inhibitor, di-butyl-para-cresol (DBPC), is added to the oil. Sunflower oil has a slightly better oxidation stability than rapeseed oil, however if a phenolic type antioxidant is added, the stability of rapeseed oil is higher. The final concentration in oil was set to 0.5 wt%, as this was identified as the optimum level.

The electro-insulating liquid from rapeseed oil that has undergone the described methods of treatment was found ready for direct use in hermetic, distribution transformers and was patented under utility number CZ 29982. It was found that the modified natural esters resulting from the aforesaid treatment fully complies with the requirements of IEC 62770 [1]. The main advantage is the possibility of using domestic raw materials with a relatively low price and suitable properties, which include biodegradability.
This oil is safe for use in distribution transformers, especially around water sources and protected natural areas.



Improving the Electrical properties

As per above results, it is now clear that the electro-insulating liquid resulting from the modification treatment has electrical properties that comply with IEC 62770 [1]. **We can further improve the electro-insulating properties of the liquid by addition of nanofillers.**

By adding nanoparticles to the natural ester oils there should be an improvement to the key electrical properties of the fluid. It should increase the flashover/breakdown voltage and dissipation factor for the fluid. By adding nanoparticles to the fluid system, it will suppress the development of an electrical charge in the liquid after an electrical potential is applied.

Nanoparticles
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Nanofiller Oxide	Purity (%)	Primary Particles size (nm)	Variation	Surface Treatment
TiO_2	>96% TiO_2	20	Hydrophilic	SiO_2
	<4% SiO_2		UV resistive	
TiO_2	99+	20		
Al_2O_3-y	99,97	20-30		
Al_2O_3-y	99,99	10		
SiO_2	>98 SiO_2			
	<2 (3-Aminopropyl)	20	Hydrophilic	(3-Aminopropyl)
	Triethoxysilan		Lipophilic	Triethoxysilan
SiO_2	99+	20	Hydrophilic	
ZnO	>98 ZnO			
	<2 (3-Aminopropyl)	30	Hydrophilic	(3-Aminopropyl)
	Triethoxysilan		Lipophilic	Triethoxysilan
ZnO	99+	20		
ZnO	99+	30		

Table 1. Overview of the selected nanoparticles to modify the new oil properties

An increase in the value of flashover/breakdown voltage is achieved as well as improved electrical properties by addition of the nanoparticles as this spreads the discharge path. The overall chemical and physical parameters of the oil are preserved even after addition of the nanoparticles.

Four nanoparticles were selected for addition to the natural esters to improve the electrical properties; which was done in review of experiments that have been conducted on mineral oils. These nanoparticles were the selected nanoparticles TiO_2, Al_2O_3, SiO_2, ZnO. Table 1 gives an overview of the selected nanoparticles.

The selection was made based on several criteria. The first is the type of nanoparticle, the second the material purity and particle size in nm, the third is the surface treatment (ST). The surface treatment is known to have a significant influence on the incorporation of the particles into the fluid system.

Results and Outcome Discussion on the Tests

Titanium Dioxide with a silica surface treatment (SFT TiO_2) has the maximum positive effect on breakdown voltage, and well at 0.25 wt%. The increase in breakdown voltage was approximately 20 kV, from 60 kV average to 80 kV average. The other nanoparticles were also added in the other tests, one type of nanoparticle ranging in concentration and particle size. The best results were achieved by the addition of titanium dioxide and well for the 20 nm size, 0.25 wt% concentration.

The increase in breakdown voltage and volume resistivity by addition of the Titanium Dioxide nanofiller at concentrations of 0.25 wt% can be explained by the creation of surface charges on the particle. These charges act against the outer electric field in the fluid, and thus the local electrical field is lowered and electron cascades from the electrode are shifted toward a higher voltage. Some studies claim that nanoparticles distributed polymers could create a “fence” effect and make the growing path of the electrical tree twist and turn like a “Z” shape, so that more energy would be consumed and therefore not available in the electrical system anymore [3].

Due to the more complicated path of pre-breakdown channels in dielectric fluids with nanoparticles, more energy is consumed and leads to the improvement of BDV, increased shallow trap density in the liquid. The shallow traps convert fast electrons to slow electrons by a trapping and de-trapping process. The hydrophilic surface can bind the water absorbed in the liquid this is in direct correlation to the type of surface treatment the nanoparticles has been subjected to. The nanofiller concentration is also an important factor, if the concentration is too high the interaction layers on the particle surfaces overlap and this will have a negative effect on the BDV.

Titanium dioxide molecule

The particle is usually covered by 5-10 H_2O molecules tightly bound to its surface, and they may absorb additional water from the oil, in which case the conductive paths may be created [4]. However, there are many variables that might contribute in minor part to changes in breakdown voltage behavior (e.g. size, specific surface area, morphology, viscosity, moisture, etc.) [5].
The dissipation factor, tan delta, was improved by the addition of ST TiO_2. The dissipation factor increases for concentrations higher than 0.25 wt%.

Points of Caution When Using Uninhibited, Untreated Natural Ester Fluids

Due to lack of oxidative stability it is recommended that the natural ester oils would only be used in hermetically sealed transformer units. The higher viscosity might cause an increase in operating temperature of transformer units, thus a design alteration needs to be done for successful long-term operation of the transformer without damage. Saturation of the cellulose pressboard system in the transformer might take longer due to the higher viscosity and higher permeability of the natural esters. Currently, there are no reliable standard test methods for analytical determination of electrical faults that might be developing in the transformer system. No fault gases or critical concentrations of individual gases has been identified. There is still a long way to go on the analytical side to get to the level of reliability testing needed for the assured infrastructure reliability needed in electrical reticulation.

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