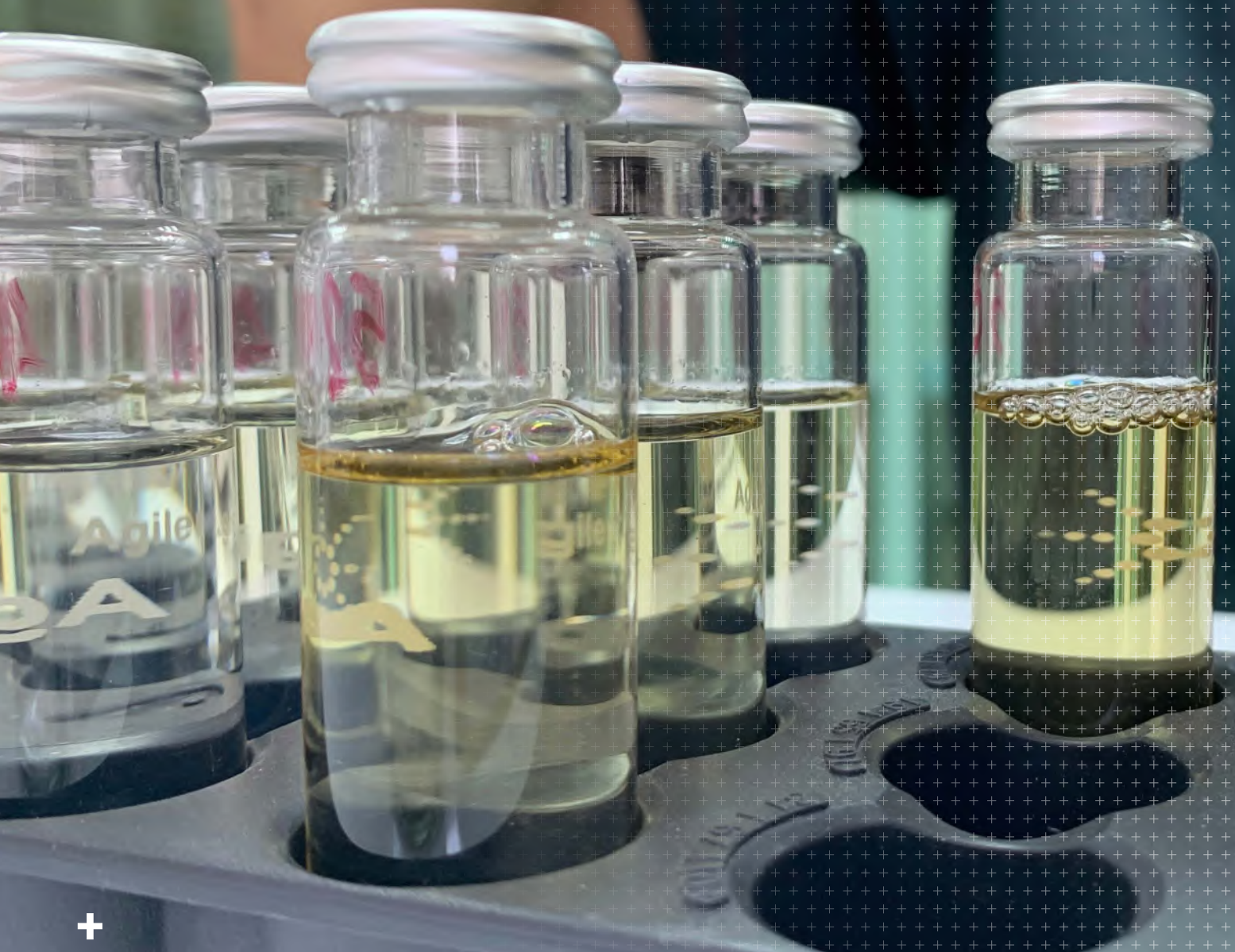


# Importance of Proper Test Protocols and Procedures for Ester Liquids

by **Rosie Lawton**  
and **Andrew Glanville**



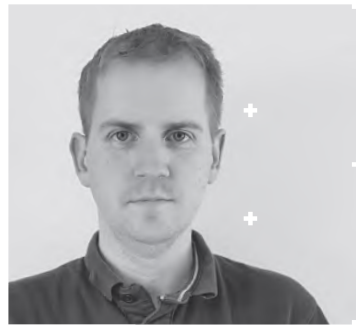
**+** Natural and synthetic esters used as transformer dielectric liquids are established alternatives to mineral oil, but there is a need in the industry for better understanding of these liquids and how they are analysed.



Photo: M&amp;I Materials

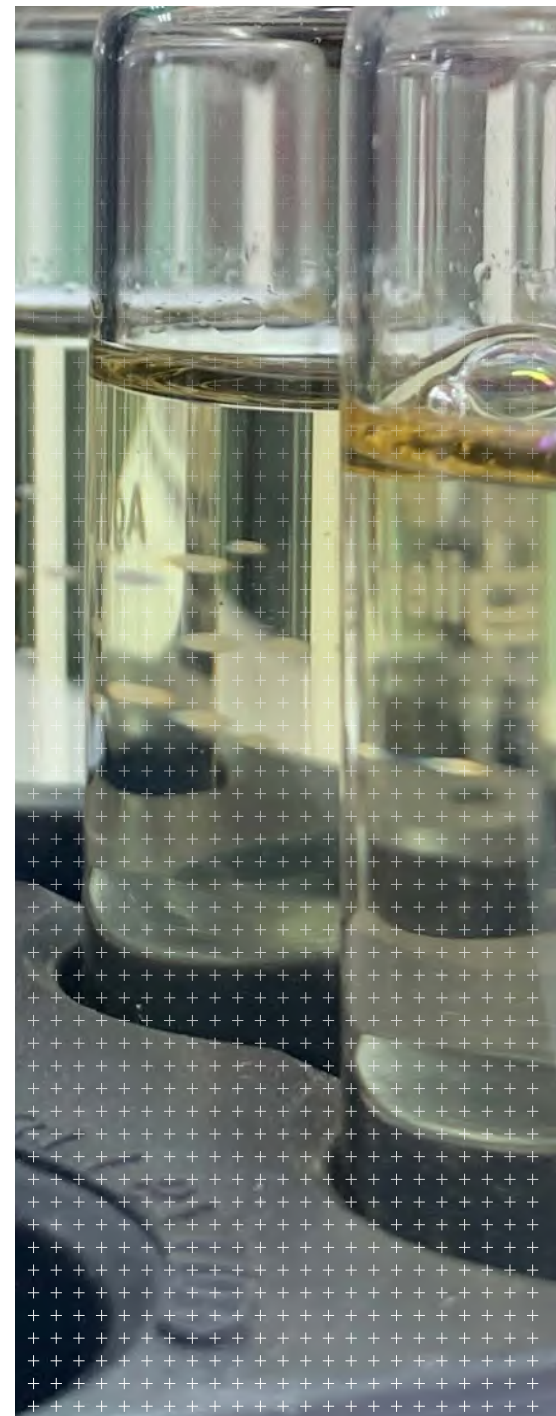


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*Although both mineral oil and ester liquids are now established in the transformer industry, it is important to note that their chemistries are quite different. As such, testing procedures outlined in various standards must be taken into consideration. Even subtle differences between synthetic and natural esters must be considered. Furthermore, variation in results provided by different laboratories can often be seen. Some of the key areas for these discrepancies include flash and fire point, dielectric dissipation factor (DDF) and dissolved gas analysis (DGA).*



*In the case of DDF, cleaning and sample preparation is significant in producing reliable results. Relatively small amounts of contamination can lead to changes in flash and fire point. In addition, inadequate cleaning leads to a build-up of carbonaceous material on the sample holder that may cause a depression in the flash and fire point. This article aims to review the differences, and the similarities, between the liquids in terms of testing and results interpretation to ensure that it is appropriate to the dielectric liquid being assessed.*

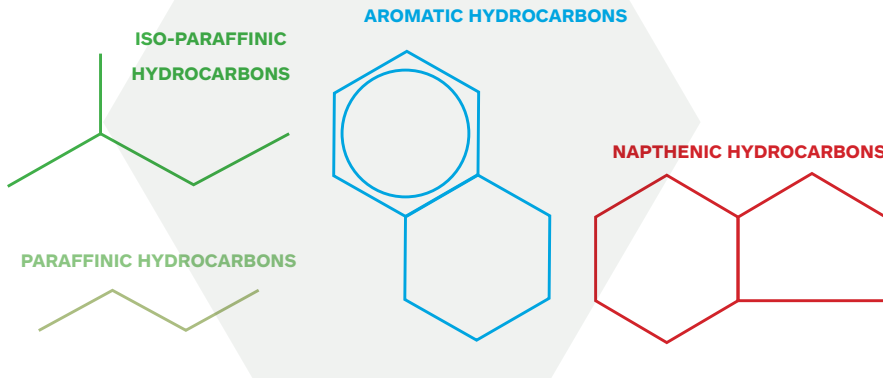


Figure 1. Structure of mineral oils

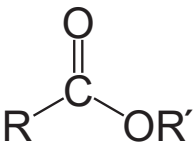


Figure 2. Structure of an ester

## Introduction

High fire safety and biodegradability are some of the key properties that have successfully established ester liquids in the transformer industry, but their chemical differences compared to mineral oil are not always fully recognised and understood. This article will highlight how care is required to ensure the test method and results interpretation are appropriate to the dielectric liquid being assessed.

Mineral oil is a mixture of paraffinic, naphthenic, or aromatic hydrocarbon structures (Figure 1), and the ratio of these structures varies leading to property differences including viscosity, oxidation stability and more. New mineral oil has minimal polar molecular content, however, during the aging process, acids and ketones are produced, increasing the overall polarity of the liquid. This leads to changes in the liquid properties such as the dielectric dissipation factor (DDF) and interfacial tension.

An ester is a chemical compound containing carbon, hydrogen and oxygen bonds arranged as in Figure 2, where R represents a hydrocarbon chain. Unlike mineral oils, ester liquids are polar to begin with, which gives esters beneficial properties such as their excellent water tolerance.

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Ester liquids can be synthetic or natural, and there are differences in their chemical structures.

Natural esters are also known as triglycerides, containing a glycerol backbone and three fatty acid chains, with the structure of the fatty acid chains influencing the ester

properties. The degree of saturation of an ester refers to the amount of double bonds present in the fatty acid chain, and these double bonds are susceptible to oxidation. Saturation also influences pour point, with highly saturated natural esters such as coconut oil having a pour point too high for use in a transformer. Currently, canola, soybean and sunflower oils are most commonly employed for use in transformers (Figure 3) [1].

Synthetic esters are a popular choice as dielectric liquids. They are created by reacting select acids and alcohols by the process of esterification. Using a synthetic ester provides a high fire point and readily biodegradability, and they have better low temperature behaviour without the oxygen stability weakness when compared to natural esters. Synthetic ester can also offer higher water tolerance due to its additional ester linkage in the structure, as shown in Figure 4.

## Interpretation of test results based on insulating liquid type

With multiple liquid types now in widespread use, correct identification of the type of insulating liquid is vital to obtaining meaningful results. This section outlines some common tests and highlights the importance of liquid identification. A small range of tests is commonly used to evaluate the quality of both unused and in-service insulating liquids for transformers. The results generated are an invaluable diagnostic tool.

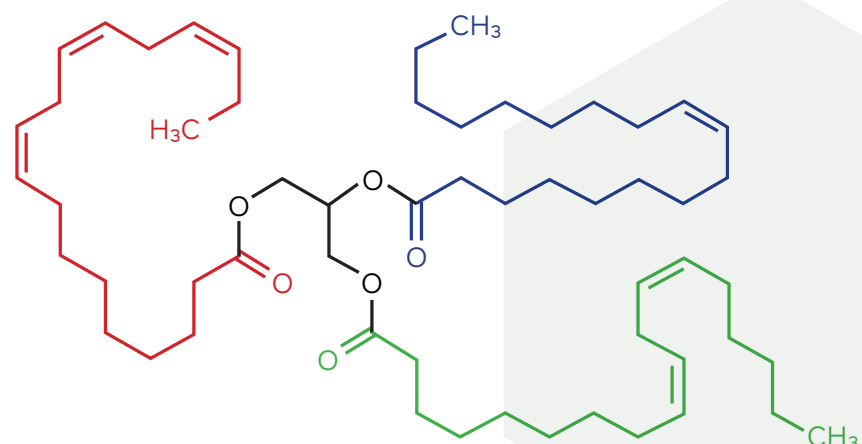


Figure 3. Structure of natural ester

Common diagnostic tests for transformer liquids include:

- Water content
- Acid value
- Dielectric breakdown strength
- Dielectric dissipation factor (DDF)
- Dissolved gas analysis (DGA)

Flash point and fire point analyses are elaborated on below as they have significant safety ramifications. Other tests, which are performed less frequently for esters, will not be explored in this article. These include interfacial tension, polychlorinated biphenyl (PCB) content, corrosive sulphur content and viscosity.

Water content is typically analysed via Karl Fischer titration instrumentation and expressed in parts per million (ppm). Due to their differing chemical structures, mineral oil and esters behave markedly different in the presence of water. Mineral oil does not readily interact with water, so relatively low levels of water negatively impact the dielectric properties of the liquid. In comparison, esters readily absorb water, and therefore higher levels may be detected (especially in service) before the same effect is apparent. For example, at 20°C, the same loss of breakdown strength is seen in mineral oil at water levels below 50 ppm, compared to over 300 ppm for natural esters, or over 600 ppm in synthetic esters [2].

Acid value is expressed as the quantity (mg) of Potassium Hydroxide (KOH) needed to neutralise 1g of the liquid. Therefore, liquids with a higher acid value (mgKOH/g) contain higher levels of acidic components. As discussed previously, the chemical structures of mineral oil and esters are different, affecting the way in which these liquids age. Mineral oil produces short chain (<C4), water soluble carboxylic acids in service that migrate with water into the solid insulation where they can cause harm. Esters produce longer chained carboxylic acids with very low water solubility.

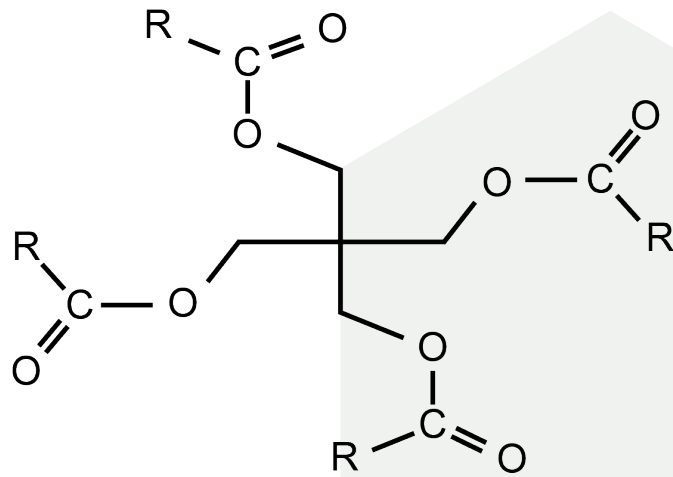


Figure 4. Structure of synthetic ester

## + With multiple liquid types now in widespread use, correct identification of the type of insulating liquid is vital to obtaining meaningful results.

This benefit alongside the superior water tolerance of esters has been demonstrated to be less harmful to cellulose materials resulting in an increased transformer lifespan, and led to a revision of industry standards so that higher levels of acid are acceptable inside ester filled transformers versus those filled with mineral oil [3].

Dielectric breakdown strength is the minimum voltage, typically expressed in kilovolts (kV), at which the liquid is forced to conduct electricity between two electrodes at a specified distance apart (e.g., 1 or 2mm for ASTM D1816). Despite their chemical differences this breakdown voltage of mineral oils and esters is similar. However, to ensure the integrity of results generated, liquid-specific differences in the testing protocols must be followed. For example, ASTM D1816 states that esters require a 15-minute stand time prior to testing whereas mineral oils require only five minutes. Failure to follow this test method requirement due to misidentification of the liquid

could lead to misleading results and unnecessary maintenance intervention.

DDF, or tan delta, is a measure of the dielectric losses in an electrical insulating liquid in an alternating electric field and of the energy dissipated as heat. Any contaminants present such as cellulose fibres, polar breakdown compounds, water, etc. increase the tendency of the liquid to conduct electricity seen as an increase in tan delta. Esters are more polar and much more hygroscopic than mineral oil, hence have inherently higher DDF without compromising dielectric performance.

DGA quantifies the level of atmospheric and fault gases dissolved in transformer liquids. Levels of these gases serve as a powerful diagnostic tool to track the health of transformers whilst in-service. The transformer liquid type has an impact on the interpretation of results as the chemistry of mineral oils and esters dictates that they interact differently with different gases. Whilst some general trends are true for the various types of liquid, other results are liquid specific. For example, in mineral oils certain levels of carbon oxides is indicative of cellulose paper degradation whereas for esters the presence of these gases is possible even in the absence of cellulose paper from the breakdown of the ester linkage in the liquid itself, so as with other analysis care needs to be taken and the liquid

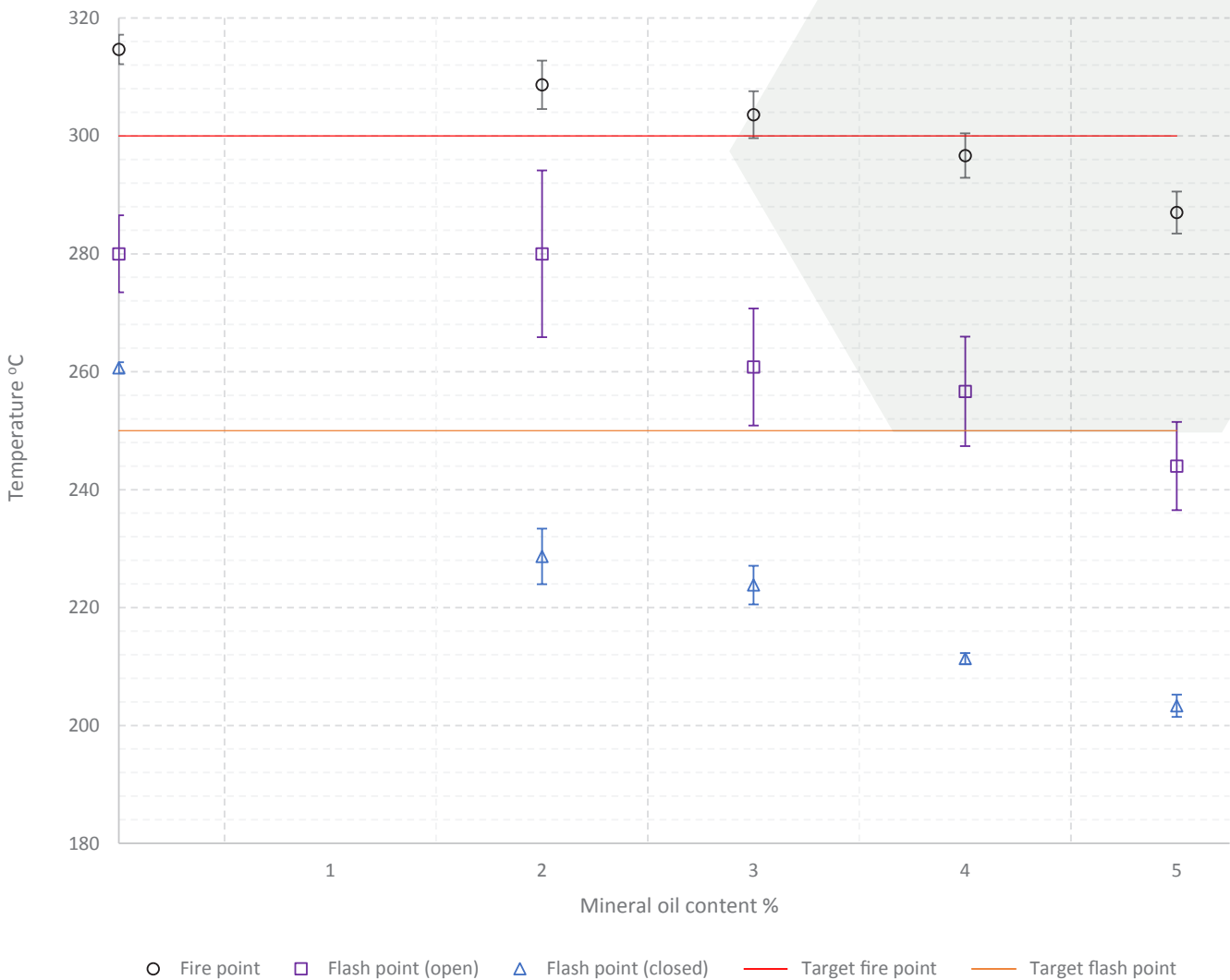


Figure 5. Fire point and flash points of MIDEI 7131 with mineral oil contamination at low concentrations

type given high precedence when interpreting results [3]. This has led to ester specific revisions to Duval's triangles and pentagons – well-established diagnostic tools which plot levels of gases simultaneously to aid interpretation of results.

Flash point is the lowest temperature at which vapours ignite in the presence of an ignition source whereas fire point is the lowest temperature at which vapours continue to burn for five seconds after the ignition source is removed [4]. Due to chemical differences in structure the flash and fire points are significantly lower for mineral oil than that of natural and synthetic esters. This is an important safety consideration. As discussed in the following section, excessive amounts of mineral oil cross-contamination can reduce the flash and fire point significantly. In refilling situations where mineral oil is replaced with

an ester, residual mineral oil above recommended levels can impact the inherent safety benefits of an ester liquid and so must be managed accordingly.

### Test procedure, repeatability, and reproducibility

In addition to interpretation of results, testing procedures are important in differentiation between different insulating liquids. Repeatability and reproducibility are also extremely important terms in the world of science and engineering. The amount of error considered acceptable greatly depends on the test and the application in question. For example, large error is not acceptable when under strict legislation or where there may be concerns for safety. By definition, repeatability of measurements refers to change measured for tests conducted under the same conditions and over

a short time. On the other hand, reproducibility refers to change measured for results obtained under varying conditions, for example different testing laboratories, instruments or even an extended timeframe.

### + Strict adherence to test procedures including cleaning and sample preparation can be crucial for producing reliable results.

Strict adherence to test procedures including cleaning and sample preparation can be crucial for producing reliable results. Transformer liquid test laboratories

commonly analyse more than one substance – mineral oil, synthetic ester, natural ester, silicone liquid or less flammable hydrocarbons. Low levels of residual contamination between consecutive tests could easily lead to variation in results. An investigation into the effect of mineral oil contamination in synthetic ester on flash and fire point was recently carried out. Interest was shown around the lower concentrations of mineral oil, particularly around the concentration that determines less flammable (fire point  $\geq 300^{\circ}\text{C}$ ) or K class (fire point  $>300^{\circ}\text{C}$ ) specification. The repeatability of these investigations was also considered. A mineral oil, used for transformer applications, was mixed with MIDELE 7131 synthetic ester at increasing concentrations. The fire and flash point were measured on both open and closed cup apparatus and each mixture was tested three times. The results in Figure 4 shows that MIDELE 7131 fire point falls below less flammable liquid specification between 3% and 4% residual mineral oil content. Previous work using

a different mineral oil with higher flash & fire point indicated that up to 3.5% mineral oil contamination was acceptable in retaining a fire point above  $300^{\circ}\text{C}$ . The repeatability in this study was very good overall. The repeatability of the flash point measured on the closed cup apparatus is much better than when measured using the open cup. This is expected and likely why the measurement using the closed cup is often suggested in various standards. In some situations, the margin of error due to the test procedure or equipment,  $8^{\circ}\text{C}$  as stated in ISO 2592, may explain why the flash point and/or fire point result is lower than anticipated. In that situation, it would be recommended to retest the sample to confirm the analysis and interpretation [4].

Flash and fire points of unused synthetic ester are often not tested however low results have been reported on several occasions, thought to be caused by improper cleaning of the pans. Contrary to expectation, no difference was found

in fire point measurements of fresh synthetic ester when the cup was not cleaned in between tests, even after excessive use seen in Figure 5. On the other hand, fire point measurements were depressed by  $\sim 7^{\circ}\text{C}$  when cups containing mineral oil had been tested but had not been cleaned before changing liquid type. A similar effect may be seen if any sample material is left on the cup rim during the analysis. Test methodology, or various apparatus brands could be responsible for the inconsistencies seen among different test sites.

Users often test DDF in new mineral oil or used dielectric liquids, which may have a detrimental effect if they then test unused ester. The polarity of ester enables the liquid to be extremely tolerant of water, but the presence of water may increase DDF values which can be falsely viewed as poor liquid condition. It is known that DDF values can be higher in ester liquids even when other testing parameters such as breakdown voltage indicate the insulating liquid is in good working condition [5].



Figure 6. Left: Cup cleaned using wire wool and solvent. Right: No cleaning of cup in between tests

Gas	Mineral oil	Synthetic ester	Natural ester
Nitrogen N <sub>2</sub>	0.091	0.091	0.074
Oxygen O <sub>2</sub>	0.172	0.152	0.134
Hydrogen H <sub>2</sub>	0.0504	0.0479	0.0471
Methane CH <sub>4</sub>	0.423	0.378	0.341
Ethane C <sub>2</sub> H <sub>6</sub>	2.88	2.2	2.14
Ethylene C <sub>2</sub> H <sub>4</sub>	1.81	1.85	1.67
Acetylene C <sub>2</sub> H <sub>2</sub>	1.25	4.26	2.58
Carbon monoxide CO	0.125	0.13	0.108
Carbon Dioxide CO <sub>2</sub>	1.1	2.08	1.54

Table 1. Gas solubility coefficients in insulating liquids from CIGRE Technical Brochure 443 [8]

The small sample volume of the test cell makes the liquid susceptible to unreliably high results as even trace contamination will affect the DDF. Recent investigations [6] showed that mixture of esters with oxidised aromatic oils resulted in abnormally high DDF. No explanation for this phenomenon was provided though it emphasises how DDF values could be unreliable when tested alongside used and different insulating liquids, especially esters. For these reasons, DDF is not recommended for monitoring the condition of an ester as a stand-alone test.

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**Although standards specifically designed for ester liquids exist, care must be taken to adhere to the correct liquid method for some testing parameters, while other parameters should be considered cautiously.**

Although DGA is not a novel technique, it remains a topic of great interest. As with other analyses, it must be recognised that the chemistry differences between

mineral oil and esters will influence results and their interpretation. As with mineral oil, correct sampling, storage, and handling is required to avoid losing hydrogen or introducing air bubbles. It has been shown that air bubbles >8% volume can reduce the hydrogen value by 35% [7]. The same test methods are used for the different insulating liquids; however, analysts must ensure the correct calibration standards are used. The gas solubility of the liquid is an important parameter related to the extraction method (headspace analysis) and later determination of the gas concentrations. The solubility of most of the gases listed in Table 1 are relatively similar for each of the insulating liquid types however it should be noted that the solubility of acetylene and carbon dioxide is much higher in ester liquids. Incorrect calibration may ultimately lead to misdiagnosis of faults in the transformer which may prove costly. A recommendation would be to have online monitoring in conjunction with periodic laboratory testing to generate a reliable trend to support operational decisions.

### Conclusion

Natural and synthetic esters used as transformer dielectric liquids are established alternatives to mineral oil. The industry calls for better understanding of these liquids and how they are analysed. DDF is highly

sensitive in esters and should only be considered together with other liquid properties. DGA is a useful tool to detect and prevent potential faults in transformers however the right calibration is important to account for differences in gas solubility. Although standards specifically designed for ester liquids exist, care must be taken to adhere to the correct liquid method for some testing parameters, while other parameters should be considered with a cautious approach.

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