ABSTRACT

Environmental considerations demand alternatives for the current mineral oils used in many electrical equipment, such as transformers. Because of their excellent biodegradability and non-toxicity, relative to petroleum derived products, the use of the vegetable oils is on the rise as insulating and heat transfer liquid in electrical devices. In addition such natural esters have a favourable lower flammability, but their viscosity and low temperature behaviour is not well suited to applications in cold climate and/or with natural cooling system. That is why a new insulating composition, based on modified vegetable oil, has been developed to present very similar properties to those of the standard insulating mineral oils and to meet the specific needs of current distribution transformers.

This article presents the formulation of this low-viscosity ester fluid, and it reports the results of the tests carried out to assess its performance in laboratory and real conditions.

INTRODUCTION

Transformers are used whenever transitions between voltage levels are needed on the electrical networks: generation, transmission and distribution. The very most widely used technology is oil-filled transformers in which the insulation is composed by cellulotic materials impregnated by mineral oil which also cools the equipment. Mineral oils have been used for decades with success because of their excellent insulating and heat transfer properties. Nowadays, to further reduce the environmental impact of transformers, research on alternative fluids such as organic esters is very active.

In this context, because of their excellent biodegradability and non-toxicity relative to petroleum products, the use of vegetable oils, or natural esters, is on the rise as insulating and heat transfer liquid in electrical devices. These natural esters have also a favourable lower flammability, but their behaviour at low temperature is not well suited to applications in cold climate and/or with natural cooling system.

Therefore EDF R&D has been commissioned to work on an original insulating liquid based on vegetable oil that can be used in distribution transformers without requiring any change in their current design and operation.

ABOUT NATURAL ESTERS

Chemistry of natural esters, triglycerides and fatty acids

Esters are ubiquitous chemical compounds, and natural esters refer to those present in plants and animals. Esters result from the condensation of carboxylic acids (R-COOH) and alcohols (R’-OH), as illustrated by the Fig. 1. Most naturally occurring esters are fats and oils, both lipids known as triglycerides.

\[
\text{Carboxylic acid} \quad \text{Alcohol} \quad \text{Ester} \quad \text{Water}
\]

\[
\text{R-COOH} + \text{HO-R’} \leftrightarrow \text{R-COO-R’} + \text{H}_2\text{O}
\]

Figure 1: Chemical reaction of esterification/hydrolysis

In organic chemistry, especially biochemistry, the triglycerides (TGs) are triesters derived from glycerol and fatty acids. Glycerol (or glycerin) is a polyol compound with three hydroxyl groups (-OH). Fatty acids (FAs) are carboxylic acids with a long unbranched aliphatic carbon skeleton (linear chain) which is either saturated or unsaturated. Naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28 (Fig. 2).

So, there are many triglycerides depending on the various combinations of the three fatty acids bonded on the glycerol backbone (therefore depending on the oil source). Conversely, all natural esters are not triglycerides because fatty acids may esterify many other alcohols than glycerol.
Properties of triglycerides

Triglycerides, and therefore fats and oils, differ in their stability, viscosity and melting point. The properties of any specific TG molecule depend on the specific 3 fatty acids that constitute it. As illustrated by Fig. 2, the FAs differ by the numbers of carbon and hydrogen atoms in the formula.

The carbon atoms, each bonded to two neighbouring carbons, form a flexible zigzagging chain. Fatty acids are high in saturated FA content and are solids; olive and linseed oils are highly unsaturated and are viscous liquids.

Moreover, double bonds being more sensitive to oxidative attack, unsaturated TGs are less stable than saturated ones, and may degrade or polymerize more easily (tendency to go rancid or to harden). That means in terms of oxidation stability, that a higher grade of saturation of the molecules corresponds to higher oxidation stability. But on the other side such high saturated TGs have high pour points and viscosity. All these chemical considerations are useful to make informed choice of the best natural esters for electro-technical applications.

FORMULATION OF A LOW-VISCOSITY ESTER COMPOSITION

The new dielectric fluid for distribution transformers has been developed in collaboration with transformer manufacturers and an oleo-chemistry research centre. The challenge was to obtain the simplest composition that meets the technical requirements for current MV/LV distribution transformers [1]. So the formulation has been optimized in order to improve the physical, chemical and electrical properties of natural esters (TGs), and thus to achieve characteristics close to those of insulating mineral oils.

The final composition is a mixture of oleic rapeseed oil (TGs) and fatty mono-esters (1:1) plus 0.3% inhibitor di-tortio-butyl-para-cresol (DBPC). The fatty esters are produced by the trans-esterification of the rapeseed triglycerides with 2-ethyl-1-hexanol. That means that the fatty acid profile of the resulting monoesters is the same as that of the TGs of the original rapeseed oil.

The Table 1 compares the main properties of this new composition with those of other insulating liquids. The ester composition has lower viscosity and pour point than those of others natural esters (i.e. vegetable oil) and this is an advantage concerning the cooling and low temperature behaviour in transformers. On the other hand the ester composition has a much lower flash point than other esters (natural and synthetic), and, as mineral oil, it cannot be classified among non-flammable liquids (Class K). Its density is comparable to that of mineral oils. Noticeable is the higher neutralization value of the ester composition, but further studies show the high acidity have no deteriorating effect on the solid insulation properties of natural esters (TGs), and thus to achieve characteristics close to those of insulating mineral oils.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test Methods</th>
<th>EC</th>
<th>VO</th>
<th>SE</th>
<th>MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity [mm².s⁻¹] at 0 °C</td>
<td>ISO 3104</td>
<td>84</td>
<td>200</td>
<td>350</td>
<td>55</td>
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<tr>
<td>at 40 °C</td>
<td></td>
<td>17</td>
<td>40</td>
<td>30</td>
<td>10</td>
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<tr>
<td>at 100 °C</td>
<td></td>
<td>4.6</td>
<td>9</td>
<td>5</td>
<td>3</td>
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<tr>
<td>Pour Point [°C]</td>
<td>ISO 3016</td>
<td>-30</td>
<td>-15</td>
<td>-60</td>
<td>-55</td>
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<tr>
<td>Flash Point [°C]</td>
<td>ISO 2719</td>
<td>175</td>
<td>290</td>
<td>270</td>
<td>140</td>
</tr>
<tr>
<td>closed cup</td>
<td>ISO 2592</td>
<td>&gt; 200</td>
<td>330</td>
<td>310</td>
<td>180</td>
</tr>
<tr>
<td>Fire Point [°C]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>open cup</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breakdown Voltage [kV]</td>
<td>CEI 60156</td>
<td>74</td>
<td>55</td>
<td>60</td>
<td>65</td>
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<td>Dielectric Dissipation Factor (tan δ) at 90 °C</td>
<td>CEI 60247</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.0001</td>
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<tr>
<td>Relative Permittivity at 90 °C</td>
<td>CEI 60247</td>
<td>2.8</td>
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<td>Density at 20 °C [kg.m⁻³]</td>
<td>ISO 3675</td>
<td>890</td>
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<td>970</td>
<td>890</td>
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<tr>
<td>Acidity / Neutralisation Value [mgKOH.g⁻¹]</td>
<td>CEI 62021</td>
<td>0.12</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
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<td>Water Saturation at 20 °C [mg.kg⁻¹]</td>
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<td>≈ 1000</td>
<td>≈ 2000</td>
<td>≈ 1500</td>
<td>≈ 50</td>
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<td>Thermal Conductivity at 20 °C [W.m⁻¹.K⁻¹]</td>
<td>ASTM D2717</td>
<td>0.22</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
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<td>Specific heat at 20 °C [kJ.kg⁻¹.K⁻¹]</td>
<td>ASTM D2766</td>
<td>2.02</td>
<td>1.9</td>
<td>1.95</td>
<td>1.9</td>
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<td>Expansion Coefficient [10⁻³ K⁻¹]</td>
<td>ASTM D1903</td>
<td>0.75</td>
<td>0.7</td>
<td>0.74</td>
<td>0.75</td>
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<tr>
<td>Ultimate Aerobic Biodegradability after 28 days [%]</td>
<td>OCDE 301 B</td>
<td>&gt; 85 readily</td>
<td>&gt; 90 readily</td>
<td>- readily</td>
<td>&lt; 40 slowly</td>
</tr>
</tbody>
</table>

Table 1: Typical data for different unused insulating fluids

EC: LOW-VISCOSITY ESTER COMPOSITION; VO: VEGETABLE OIL (TGs); SE: SYNTHETIC ORGANIC ESTER; MO: MINERAL OIL.
(cellulose). This is a major difference to mineral oils. At last, its environmental features stay alike those of vegetable oils, i.e. far better than mineral oil ones.

LABORATORY INVESTIGATIONS

Compatibility with other transformer materials
Any new insulating liquid must be investigated about compatibility prior its use in equipment. So tests with transformer materials immersed in the ester composition have been performed by several manufacturers, and the results compared to those with mineral oils and/or synthetic esters. The ester composition is found compatible with most of varnish, painting, coating or enamelling materials used to protect or insulate metals; it has no influence on metals themselves (non corrosive). Most polymers, elastomers and resins are also compatible with the composition, but some nitril rubber, polyamide or polyester accessories should be selected carefully. [2]

Absorption in thick cellulose materials
An important parameter for the construction of transformers is the impregnation of the cellulose insulation. As the viscosity of the ester composition differs from those of standard mineral oils, investigation of its impregnation behaviour was necessary. Three different insulating materials have been tested: pressboard, laminated board and laminated wood. The results show that the low-viscosity ester composition concerning the oil absorption in the tested solid materials is slightly better than that of a synthetic ester which is already used in transformers. [2]

Ester and paper ageing
The oxidation stability assessment of insulating liquids is an important issue, especially in the case of natural esters which are intrinsically less stable than petroleum products. One way to address this matter is to compare the performances of esters and mineral oil submitted to the same ageing protocol. As there is not yet a standard test method applicable to both types of insulating liquids, a specific ageing test has been established. The results show that the evolution during ageing of the ester fluid characteristics does not diverge from those of the mineral oil. The baseline values and evolutions magnitude differ, but their trends do not. The acidity and water content, higher in the new vegetable oil, tend to increase less quickly than they do in mineral oils. The mechanical properties of the cellulosic materials after ageing are comparable but, taking into account the overall tendency, the paper ageing in transformer filled with ester composition could be lower on the long term. [3]

Gassing behaviour
The low-viscosity ester composition shows, like most insulating natural esters, a stray gassing which is connected with the oxidation stability of the fluid and is dependent on temperature. Transformer materials such as copper have also an influence on the gas production, probably connected to peroxides formation/destruction. Hydrolysis and oxidation reactions involving natural esters can have a high impact in the development of carbon oxides. Carbon monoxide is produced by both mineral oils and natural esters mainly through thermal degradation of the insulating liquid itself. With mineral oil, carbon dioxide ($CO_2$) derives mainly from the cellulose insulation; while natural esters show a $CO_2$ formation depending on the thermal endurance of the liquid itself.

One notes that ester fluids develop higher concentrations of ethane ($C_2H_6$) than mineral oil (likely produced by oxidation of specific unsaturated FAs). Thus ethane can be regarded as a key-gas for the interpretation of dissolved gas analysis (DGA). [2]

Thermal characteristics and heat transfer performance
In addition to the dielectric role, the insulating fluids have to ensure the cooling of transformer in order to maintain acceptable temperature and thus a normal ageing. The heat removal, from coils towards the outside of transformer, by the fluid is driven by the following thermo-physical properties: kinematic viscosity, specific heat (or thermal capacity), coefficient of expansion and thermal conductivity. The table 1 shows that these properties differ from one fluid to another. Simulations carried out using a network thermo-hydraulic model on a typical disk winding indicate that, in forced oil convection mode, lower temperature rise could be expected by using ester fluids and, in natural oil convection, the low-viscosity ester composition (and synthetic esters) behaves better than vegetable oil. [4]

EXPERIMENTATION WITH MV/LV DISTRIBUTION TRANSFORMERS
The laboratory tests show that, compared to other insulating natural esters (i.e. vegetable oils or TGs), the low viscosity ester composition is very similar to standard mineral oils regarding their physical and thermal properties, and it seems to behave the same way inside transformers. So, this insulating fluid appears well suited to replace mineral oil in MV/LV transformers without requiring any design or manufacturing modifications, as expected.

Transformers and testing
The typical transformers used by the French DSO are 20 kV / 410 V with ONAN cooling design (no pump or fan). To assess the behaviour of the low-viscosity ester composition in real conditions, 12 of such transformers (from 50 to 400 kVA) have been provided by four manufacturers after they have been filled and hermetically sealed (no $O_2$ and moisture ingress) in
factories with this liquid without any additional modification. These standard transformers were then installed on the French distribution network and monitored during several years. Chemical analyses and electrical testing of samples of the fluid in service have been carried out to investigate the degradation of the ester composition and cellulosic insulation. The feedback shows no significant changes in the liquid characteristics, and no operation problems have been reported so far.

**Test results**

Only general trends of the salient properties that differ from those of mineral oils are discussed here (see [5] for further information). Note that all values are acceptable according to the IEEE C57.147 Guide about natural esters in transformers.

**Water content**

The water contents in esters are higher than in mineral oils (about one order of magnitude) due to its higher water solubility in esters. But measured values remain far below the saturation (> 1000 ppm) as confirmed by the lack of negative impact on the breakdown voltage. The outstanding feature of the water content evolution is the drying of the ester composition within the first year. After this period, water contents increase but seem to remain below the initial ones. This behavior is probably linked to the setting up of dynamic moisture equilibrium between ester fluid and solid insulation inside transformers.

**Viscosity**

It is known that the viscosity of ester fluids may increase over ageing (because of oligomerization of fatty esters due to abnormal exposure to air and heat). Experimental data do not show such evolution and the viscosities of the ester composition remain unchanged after 2 years and more in operation.

**Acidity and free alcohol content**

The oxidation stability of insulating fluids is classically evaluated by acidity measurements. Esters may oxidize but they can also degrade by hydrolysis that releases acids and alcohol (see Fig. 1). So acidity measurement seems relevant here, even though the standard test method (IEC 61125-1) developed for mineral oil is not optimized for ester fluids. Finally, the results show satisfactory acidity values and specific analyses do not reveal production of free-alcohol.

**Other analyses**

Furanic content and dissolved gas analyses (DGAs) have been carried out on some samples of esters in order to consider the degradation of the insulating papers and pressboards. But, in the absence of validated and reliable feedback, the interpretation of the results is not really possible. Nevertheless, all furanic contents are below the detection limit of the analytical method, indicating that cellulose does not degrade significantly. And DGAs confirm the prevailing productions of ethane and hydrogen.

**CONCLUSION**

Because additional costs are not affordable for MV/LV distribution transformers, and because reducing their environmental impacts is desirable, the low-viscosity ester composition presented here appears to be an promising alternative to current insulating mineral oils. This unsophisticated (thus cheap) ester composition has been designed to have functional properties similar to those of mineral oils, and to remain as readily biodegradable and non-toxic as vegetable oils are. The investigations indicate that this composition performs the main functions expected of an insulating and cooling fluid in distribution transformers. Furthermore, the tests in real transformers in real conditions do not reveal any problems regarding its behaviour and ageing. And five years after the transformers were energized; no incidents have been reported. All these results confirm the suitability of such a low-viscosity environmental-friendly insulating fluid for MV applications.

We are now witnessing attempts to extend its use in higher power transformers but further detailed researches and another approach are required.

**REFERENCES**


