A Comparative Study of the Chemical Stability of Esters for Use in Large Power Transformers

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Abstract: There is uncertainty as to whether ester oils will be suitable replacements for mineral oil used in large free breathing power transformers, such as those found on the transmission system of the UK. This is partly due to concerns regarding the chemical stability of esters and how stability will affect the dielectric properties of the oil. This paper presents research investigating how ester dielectric properties change due to the effects of ageing compared to mineral oil and seeks to advise Utilities which parameters to monitor in service. This investigation considered the dielectric properties of AC and impulse dielectric strength, dielectric dissipation factor and acidity. It is recommended to monitor trends over working life rather than simply comparing values, and to use at least two parameters including the dielectric dissipation factor and acidity.

Introduction

This project has been funded by industry to investigate whether esters are suitable for new or retrofilled free breathing power transformers of up to 400kV. The investigation methodology has been to define those factors that influence the oils and insulation, conduct laboratory based experiments and then to determine how the esters have performed.

One such factor is insulation ageing, leading to eventual equipment failure. The intended transformers are free breathing, and although the breathed air is kept dry, the oil is exposed to the oxygen in the air, thus potentially increasing the rate of oxidation and thus ageing.

Power transformers typically use oil and cellulose as insulation. Transformer specialists state that cellulose is the weakest link in the transformer insulation due to the fact that it cannot easily be replaced, whereas the oil can be changed or reprocessed. There is also a consensus of opinion that the oil quality is important, as by-products formed during oil ageing, such as moisture and acids, affect the rate of cellulose degradation. When insulating oil degrades, the problems can usually be divided into two areas:

1. By-products may affect long term operation of transformer, e.g. increased cellulose degradation
2. Worsening performance of oil as an insulator, e.g. reduced dielectric strength

There are two types of ester, natural and synthetic. Natural esters are generally cheaper to produce than their synthetic counterparts; however they are more prone to oxidation due to the differences in chemical structure.

It has been shown that natural esters can effectively extend the life of cellulosic insulation, which is of interest to the Utilities [1]. The mechanisms proposed reduce the water in the cellulose by the:

- hygroscopic nature of esters to absorb moisture from the cellulose
- hydrolysis of the ester to consume moisture
- transesterification of the ester to protect the cellulose from moisture ingress.

Acids affect the rate of cellulosic degradation. ZTZ Service believes that acids formed in mineral oil are detrimental [2], while Cooper Power Systems (CPS) considers that acids produced by esters are beneficial [1]. This is accounted for by differences in the chemical structures of acids formed from esters and mineral oil. If ester-filled transformers are to operate for longer, as suggested by CPS, condition monitoring will be essential to ensure that the oil quality is maintained.

Therefore the Utilities need to be made aware of which parameters to monitor for oil degradation and not mistakenly record and react to the beneficial processes.

Several papers have been found on the ageing of esters. To date, CPS have focussed on demonstrating the stability of esters in sealed environments, which exclude air. Oommen [3] and Lewand [4] have individually reported unsatisfactory results when ageing certain natural esters using the ASTM D2112 Rotating bomb and ASTM D2440 Oxidation Stability tests and noted that the ester tended to gel. However, Lewand reports that the manufacturer feels that the oxidation method used was developed for mineral oil and does not reflect the actual performance of the ester in field service. Borsi aged samples of synthetic ester in open vessels at 150°C for 1000 hours with copper, steel and aluminium chips. It was concluded that there was no significant reduction of breakdown strength compared to silicone oil, even though the dielectric dissipation factor increased by two decades. However, the ester specimens had high moisture contents (~1100ppm), which may have affected the results [5].

Oxidation may change the oils, forming polar groups and acids. Esters may be affected by hydrolysis in the presence of moisture forming acids. Although it is proposed by the manufacturer that ester hydrolysis is beneficial for the cellulose insulation, it is not known at present whether further, undesirable, reactions of hydrolysis products will take place due to oxidation.

Biological action in normal use could not be investigated in this experiment, as high temperatures would kill off any organisms and prevent such action. However,

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research performed by CPS suggests that organisms are unlikely to exist in a transformer tank as this environment is too dry to permit growth [6].

This paper presents the change in properties of ester oils compared to mineral oil after ageing at elevated temperatures in the presence of materials typically found in transformers, which may act as catalytic agents. Examples of a synthetic polyol tetraester and a seed based natural ester have been used. Both esters are commercially available. As this is a comparison, it is not meant to indicate the number of years that an ester will be effective as an insulator in the field. It would be difficult to extrapolate the rate of reaction to transformer operating temperatures, as the temperature profile of the oil will be dependant on loading, which will change throughout the day and year, localised hot spots around conductors and temperature changes due to circulation.

Investigation

The aim of these investigations was to monitor changes in stability and to advise the Utilities which parameters to monitor during service. A range of dielectric and chemical factors were selected for measurement. These consisted of: AC breakdown voltage (BAUR DPA75), lightning impulse breakdown voltage (Haefely impulse generator), dielectric dissipation factor (Eltel ADTR-2K), acidity (Metrohm 686 Titroprocessor & 665 Dosimat) and moisture content (Metrohm 684 Coulometer & 832 Thermoprep oven).

Care has to be taken when interpreting data. Lewand notes "It must be emphasized, however, that the properties of a natural ester cannot be correlated directly to that of a mineral oil as the chemistries of the two types of liquids are very different" [7]. An example of this is the tan δ. The tan δ of oil is related to the number of polar groups in the oil. Any change in this parameter can give an insight into the deterioration of the oil. Chemical reactions during ageing produce polar groups and increase the tan δ. However the tan δ only provides an indication of the quantity of polar groups in oil, not their aggressive–nature or impact on transformer insulation. As esters have different organic structures to mineral oil, it is evident that different types and quantities of by-products may be created during degradation.

Samples of mineral oil and ester were heated to 115°C for up to 28 days. The ageing method was similar to ASTM D1934 in that open bottles were used with different items as potential catalysts. A decision to use open containers was made to represent a free breathing transformer and allow contact with oxygen in the air. Combinations of copper and glass coated core steel were used. The glass coated steel was from transformer production waste. Pressboard was not used because there was a concern that pressboard could absorb by-products from the oil and distort the results. An air circulating oven was used. After ageing, the bottles were immediately sealed and left to cool naturally. Bottles were removed after 7, 14 and 28 days then discarded after measurements.

Results

Moisture levels were measured to explain any peculiarities with breakdown voltages due to the fact that the dielectric strength is known to be affected by moisture. Measurements involved collecting several millilitres of oil in a glass vial and heating the vial to 140°C. The resultant gases were collected and passed into the reagent chamber to measure the amount of moisture. It was noted that when the natural ester was aged with copper, the Karl Fischer titrations did not reach their end points. The manufacturer was consulted and believes that this was due to the Karl Fischer reagent being unsuitable for use with the by-products created during ester oxidation. This is further evidence of chemical degradation in the natural ester.

AC Breakdown voltage comparison

A Baur DPA75 was used for AC breakdown voltage measurements based upon ASTM D1816 using partially spherical electrodes and a 1mm gap. In total 4 samples of 5 breakdowns gave 20 points of data. Care was taken to allow sufficient time for air bubbles to escape when pouring the esters into the test cell. It should be noted that ASTM D1816 has not been verified for oils over 19cSt at 40°C viscosity, and that esters are even more viscous. However CPS believes that this standard is still suitable using a longer stand time after pouring, and recommend a 15 minute stand time [8].

The dielectric strength of an oil is related to the moisture content of oil. The difficulty when comparing breakdown voltages of different samples of the same oil is that if moisture levels are too dissimilar, differences in dielectric strength may be incorrectly attributed to chemical transformation and not moisture content, particularly when the oil cools and reaches its saturation limit. Drying the oil to the original moisture content may be difficult. During chemical degradation, water may be chemically attached to the aldehydes, alcohols and acid groups which are created and this attached water cannot be readily removed by temperature and vacuum [9]. Neither mineral oil nor synthetic ester had high moisture contents in terms of relative humidity. Unfortunately, the moisture content of the natural ester was not known because of the problem with the Karl Fischer reagent.

Table 1: Moisture contents of oils (ppm)

Ageing time	7	14	28
Mineral oil	13	9	12
Synthetic ester	26	18	37
Natural ester	-	-	-

Both esters maintained their dielectric strength during ageing. The variations in breakdown voltage may have been caused by different levels of moisture, insoluble ageing products and small breakdown voltage sample sizes (Figure 1). This result may infer that it is not the ageing of the oils that affects the transformers. It is important therefore to show if the ageing materials produced by the oils create an enhanced rate of cellulose ageing.

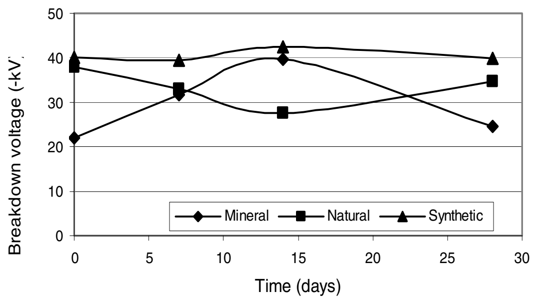

Figure 1: Breakdown voltages of oils heated with copper and steel

Lightning impulse breakdown voltage comparison

A Haefely 10 stage impulse generator was used, in a 6 stage configuration, to provide a 1.2µs/50µs negative voltage waveshape, which simulates a lightning strike according to ASTM D3300. Normally ASTM D3300 is used for oils of petroleum origin, however ASTM D6871, the specification for natural ester fluids, makes the recommendation to use this standard. A test cell with 12.7mm diameter spherical to spherical brass electrode configuration with 3.8mm gap was used. A low voltage transient was applied and raised in steps of -10kV until 5 flashovers were observed. Samples heated with copper for 28 days were compared with samples of new oil. It is noted that new mineral oil had an impulse breakdown voltage around 10 – 20% higher than new esters (Figure 2). However, mineral oil breakdown voltage tends to decrease at a faster rate than that of the esters, with no noticeable reduction in the synthetic ester breakdown voltage. It is noted that the lightning impulse voltage was raised in steps of -10kV, so the true breakdown voltage may be up to 10kV lower than measured.

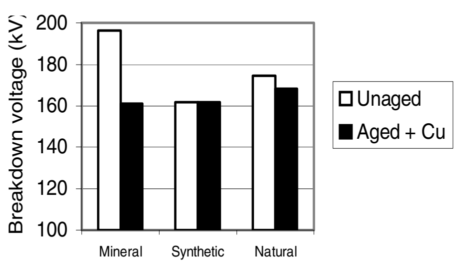

Figure 2: Lightning impulse breakdown voltage of oils

Acidity

Acidity is one measurement used to assess the degree of oil degradation. The inclusion of copper gave different results for the natural ester than the mineral oil, as shown in Figures 3 and 4. The inclusion of copper increased acid production in the mineral oil, however the acidity of the natural ester is lower with the presence of copper. CPS suggested that without copper, hydrolysis had occurred which would be beneficial to the cellulosic insulation, as it would effectively reduce its moisture content.

CPS also suggested in this investigation that with the presence of both copper and air, oxidation was the primary mechanism creating hydroperoxides, these then formed aldehydes and ketones, which have little or no acidity. The possibility of the peroxide reaction is backed up by Sabau [10]. Although no increase in acid was noted during this investigation, CPS believe that if ageing continued, the acidity would increase due to the by-products eventually forming acids.

The synthetic ester appears stable in the presence of copper, experiencing neither hydrolysis nor oxidation. As previously stated, acidity only provides the quantity of acids present in the sample, not the aggressive nature it may possess. Acidity is important as it affects the rate of cellulose degradation. As there is evidence to suggest that acids formed from hydrolysis of the ester are beneficial to the cellulose, and that acids formed from oxidation of mineral oil are detrimental, care must be taken when comparing the different acidity measurements.

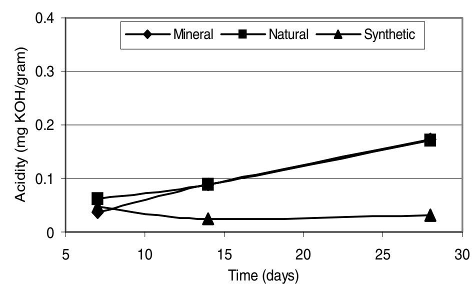

Figure 3: Change in acidities of oils heated without copper

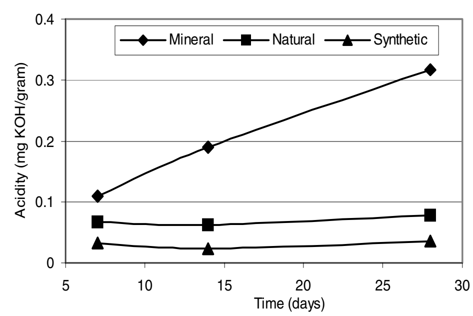

Figure 4: Change in oil acidities with copper catalyst

Dielectric dissipation factor (tan δ)

All measurements were taken at 25°C ± 1°C. When oil was poured into the test vessel, time was allowed for the air bubbles to escape. The most pronounced trend in tan δ was with the natural ester aged with copper, most likely due to the presence of ketones and aldehydes (Figure 5). The graph was replotted without the natural ester with copper to display in more detail the tan δ trend of the other samples

(Figure 6). As stated earlier, it is not advisable to compare levels of tan δ between oils due to their different chemistries, however the rate of increase appears to be a good indication as to whether degradation is occurring.

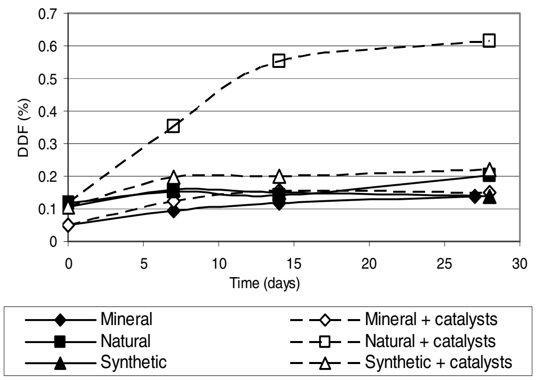

Figure 5: Dielectric dissipation factor of oils

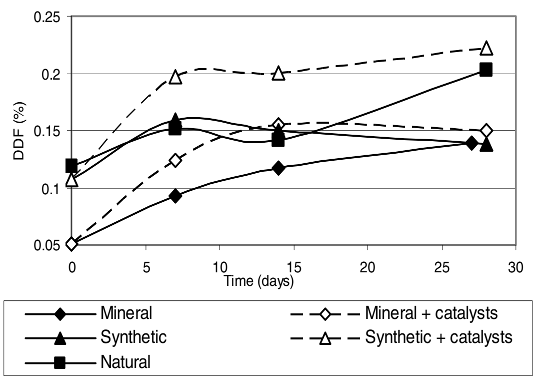

Figure 6: Dielectric dissipation factor of oils replotted

While acids should increase the tan δ, it is noted that the tan δ is not strictly proportional to the acid increase due to other non-acidic polar compounds forming during degradation. There is a general relationship that if the acidity of an ester increases while the tan δ is fairly constant, this may be due to hydrolysis. Alternatively, if the acidity remains fairly constant while the tan δ increases, this may be due to oxidation.

Conclusions

Condition monitoring of the oil in power transformers during their service life must be based upon several different properties and not on a single parameter. If the natural ester is exposed to air, then both acidity and tan δ measurements should be performed in order to assess the quality of the oil and distinguish between hydrolysis (increasing acidity with constant tan δ) and oxidation (increasing tan δ with constant acidity). Given that no change in acidity was observed with the synthetic ester it is difficult to state whether this conclusion applies to all esters. However Borsi noted an increase in tan δ for the synthetic oil when heated at 150°C so it may be applicable. Ester breakdown voltages have remained constant during heating, indicating that in this investigation hydrolysis and oxidation have not had a major influence on the dielectric strength of the oil.

Future work

Unfortunately, these measurements only determine the overall quantity of polar groups, acids etc present in the oils. No qualitative information on the exact nature and impact on the insulation is yet known. Future work would involve defining the by-products that are created and their individual impact on the performance of the transformer. To date, CPS has only reported the effect of ester by-products on cellulose ageing. If esters do reduce the rate of solid insulation ageing, which is regarded as the weakest link in transformer insulation, it may be that another type of transformer insulation fault could become prevalent.

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