Comparison of the mineral oil lifetime estimates obtained by differential scanning calorimetry, infrared spectroscopy, and dielectric dissipation factor measurements

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ABSTRACT

In this study, improved observables and new endpoint criteria were developed to assess the remaining useful life of mineral transformer oil using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). The tested oil was exposed to thermal ageing at temperatures of 110, 120 and 130 °C for times ranging from 100 to 2400 h. The intensity of the infrared spectral band of the low-temperature inhibitor and the temperature of the thermo-oxidative DSC peak were considered for evaluation. The obtained results were correlated with standardized dielectric dissipation factor (tan δ) measurements. The results indicated that the analysed observables changed continuously during the applied thermal ageing. The endpoint criteria were subsequently determined and Arrhenius diagrams were constructed. The results demonstrated that the determination of the actual state or the lifetime of the transformer oil via DSC or FT-IR may be beneficial in terms of reducing the measurement time, the influence of moisture on the measurement results and the oil volume required for the tests. Thus, DSC and FT-IR represent promising alternatives to dissipation factor measurements.

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1. Introduction

Estimating the lifetime of mineral oils used in power transformers is an essential practice for oil producers. Given that the power transformers are the most expensive parts of an electricity supply system, their planned service lifetime is several decades under standard operating conditions. Transformer insulating systems formed from a mineral oil and craft paper are considered the most sensitive to ageing [1,2]. Although the paper part cannot be easily repaired during the planned service lifetime [3], the actual state of the oil part itself is typically monitored continuously. The residual lifetime of the oil can be estimated based on the initial properties of the mineral oil and its actual values. Then, the electricity network operator can decide whether to recover or replace the liquid part of the power transformer. For this reason, the transformer oil is often used for diagnostic purposes [4,5].

It is impossible to estimate the degradation lifetime of mineral oil at common operating temperatures because the necessary tests are time intensive and economically unacceptable; thus, accelerated ageing tests, in which the tested oil is exposed to an increased

temperature load, are typically used [1]. Temperature is one of the primary degradation factors for most engineering materials, and it can accelerate the physical and chemical degradation processes within the material structure [6].

The established methodology for estimating the lifetime of a material used for electrical applications is found in the international standard IEC 60216 [7], which defines all required test procedures. The standard requires not only the appropriate monitoring of parameters (observables) but also the proper selection of the endpoint criterion. The endpoint criterion is generally estimated based on accelerated ageing procedures and the application of the Arrhenius model. At minimum, samples should be aged at three increased temperatures compared to the operation temperature, and a sufficiently sensitive measurement method should be applied until the endpoint criterion is achieved or the sample is destroyed (based on the used method) [8]. The endpoint criterion is defined by standards when the commonly used methods are used; in other methods, the recommended practice [7] is to declare the endpoint criterion as the value corresponding to the worsening of the monitored parameter by 50% of its original value. In other cases, it is also possible to use alternative endpoint criterion appropriate to unacceptable worsening of the monitored parameter.

Measuring the dielectric dissipation factor (tan δ), which is one of the most frequently used methods for these purposes [2,9–13],

has several disadvantages when analysing transformer oil; for instance, the measurement is time intensive, the results can be affected by humidity and the measuring procedure requires a fairly large volume of the oil (at least 120 ml for one test). Thus, there is a need to investigate novel methods of evaluating new observables and determining the endpoint criteria [14].

For these reasons, this paper presents potential observables and new endpoint criteria for determining the residual lifetime of cycloalkane-based mineral oil using two different analyses: differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR), over the course of long-term accelerated thermal ageing at various temperatures and times. Along with DSC and FT-IR, tan δ measurements were also determined as a reference measurement for the purposes of this study.

2. Theory of thermo-oxidative ageing of mineral oils: assumptions

Transformer mineral oil contains a mixture of different hydrocarbons but is generally composed of three main components: alkanes, cycloalkanes and aromatic hydrocarbons. Alkanes include saturated linear (normal) and branched (iso-) alkanes, cycloalkanes with side hydrocarbon chains and aromatic hydrocarbons contain unsaturated discrete or condensed aromatic rings that may have side alkyl- or cycloalkyl substituents [15]. The ratio of these three components is variable and determines the oil properties.

As noted above, the tested mineral oil was of the cycloalkane-based type, which contains a relatively low ratio of iso-alkanes to cycloalkanes and virtually no linear alkanes. Cycloalkane-based oil, as with the other oil types, is oxidized by a free radical chain mechanism that has already been described by many authors (e.g., [16,17]). At low temperatures (30–120 °C), radical chains are initiated by the attack of the dissolved oxygen on hydrocarbons in the presence of catalysts (metals, aromatic compounds) when peroxy- and alkyl radicals are formed. The rate of initiation is extremely slow [16]. After their formation, alkyl radicals are extremely reactive and react with oxygen to form alkyl peroxy radicals:

$$R(CH_3)CH^\bullet + O_2 \rightarrow R(CH_3)CH-OO^\bullet \tag{1}$$
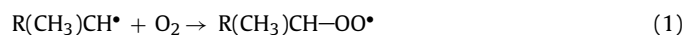
This reaction leads to the formation of a hydroperoxide and an alkyl radical that can again react with oxygen. Termination may be caused by the disproportionation or rearrangement of radical species, which yields ketones and alcohols. Radicals can recombine if the oxygen concentration in the liquid is limited. In summary, the low-temperature oxidation of hydrocarbons leads to the formation of alkylhydroperoxides (ROOH), dialkylperoxides (ROOR), alcohols (ROH), aldehydes (RCHO) and ketones RC=O [16,18].

At temperatures higher than 120 °C, the initiation and propagation reactions are the same as described under low-temperature conditions, but the reaction rate is faster. In addition, the decomposition reactions of hydroperoxides play an important role during the high-temperature oxidation process [16,19]. The cause is high activation energy, which is required for the homolytic cleavage process of hydroperoxides to an alkoxy:

$$ROOH \rightarrow RO^\bullet + HO^\bullet \tag{2}$$

Once formed, hydroxy and especially alkoxy radicals are sufficiently active that they abstract hydrogen atoms in non-selective reactions:

$$HO^\bullet + CH_3-R \rightarrow H_2O + RCH_2^\bullet \tag{3}$$

$$HO^\bullet + R-CH_2-R^1 \rightarrow H_2O + R(R^1)HC^\bullet \tag{4}$$

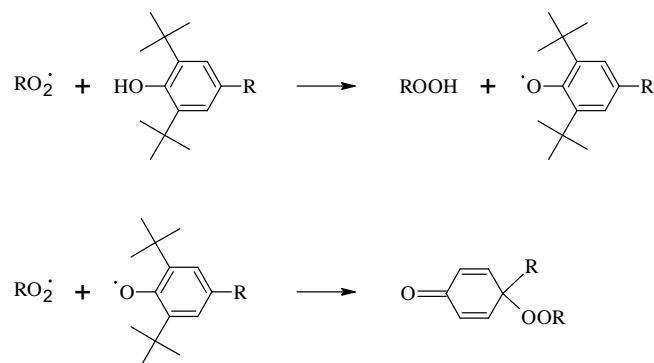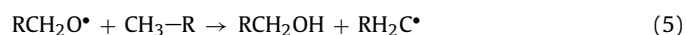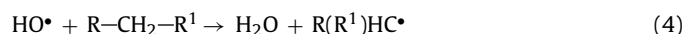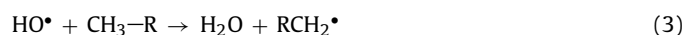$$RCH_2O^\bullet + CH_3-R \rightarrow RCH_2OH + RH_2C^\bullet \tag{5}$$

Fig. 1. Antioxidant action of the sterically hindered phenols; R indicates a hydrocarbon residue [24].

Carboxylic acids (RCOOH) are also formed through the oxidation of aldehydes. In a subsequent step, they can react with alcohols to form esters (RCOOR) [15,16].

At higher ageing temperatures, the viscosity of the oil gradually increases [20] as a result of the polycondensation reactions. Further polycondensation and polymerization reactions yield products that are no longer soluble in the oil. The resulting precipitate is called sludge. In these reactions, low-molecular-weight volatile products are formed (e.g., CO_2, CH_2O, CH_3OH) along with large quantities of water. All described oxidation products are polar molecules. The increased concentration of polar substances in oil causes higher dielectric losses, reduced electrical resistance of the insulation system and higher solubility of water in oil [21,22].

The addition of antioxidants is the most convenient and effective way to block the thermal oxidation of oils. 2,6-Di-tert-butyl-4-methylphenol, also called 2,6-ditert-butyl-*p*-cresol (DBPC) or butylated hydroxytoluene (BHT), is the most frequently used antioxidant in not only insulating oils but also in foods containing fats, pharmaceuticals, petroleum products or polymers [23]. BHT belongs to so-called hindered phenol species, which contains a hydroxyl group sterically hindered by two bulky tert-butyl substituent groups. Hindered phenol antioxidants work as radical scavenger antioxidants, which intercept and react with free radicals faster than hydrocarbons. Antioxidants donate hydrogen to the free radicals, becoming radical themselves (see Fig. 1). The resulting phenoxy radicals have low reactivity due to resonance stabilization through their aromatic ring systems and cannot attack the oil molecules. These radicals are transformed into quinonoid structures, which are stable up to approximately 120 °C [16,24].

We can assume that all processes described above affect the potential observables and endpoint criteria and, hence, the method used to determine the residual lifetime of the transformer mineral oil itself.

3. Brief theory of measuring the dielectric dissipation factor

A detailed description of the theory of the dissipation factor and dielectric losses has been described elsewhere [25–27]. Generally, the dissipation factor is closely related to dielectric losses and thus provides a measurable quantity representing the amount of energy that is dissipated as heat in a material placed in an external electric field. Dielectric losses are influenced by electrical conductivity and the various mechanisms of dielectric relaxation that appear when electric dipoles are influenced by an applied electric field. Every insulating material is characterized by an intrinsic dissipation factor value that is governed by its chemical composition, structure, and operational environment. Subsequent deterioration processes, such as thermal ageing, will increase dielectric losses; thus, obser-