



The spontaneous ionic purification phenomenon of transformer oil: Presentation and consequences

J.C. Filippini^{a,b,*}, R. Tobazéon^a, Ph. Guuinic^c, O. Moreau^c

^aIRLAB, 12 rue André Rivoire, 38100 Grenoble, France

^bLEMD, CNRS/UJF, BP166, 38042 Grenoble Cedex, France

^cEDF R&D TESE, 1 avenue du Général de Gaulle, 92141 Clamart, France

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ABSTRACT

Experiments performed on different oils from in service transformers show that the conductivity of these oils can significantly decrease as a function of the time elapsed from the instant at which the test cell was filled up. Material for a characterization of this phenomenon – called “spontaneous ionic purification phenomenon” – is presented and a route for interpretation is proposed. The consequences of this phenomenon on the oil characterization are examined.

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1. Introduction

The electrical conductivity of insulating oils is an important characterization parameter for new oils and for oils from in service transformers. The conductivity is proportional to the electrical charge density in the liquid at thermodynamic equilibrium. It is the image of its ionic purity and its variations during the transformer life can reveal a significant evolution of the insulation.

It seems presently accepted that the conductivity of insulating oils is a well-defined parameter, easily measured as new reliable techniques are now available [1]. The experiments which will be described in this paper show that it is not the case. Using the alternate square wave method [2] we showed that the conductivity of certain oils, measured at room temperature in a stainless steel test cell, can decrease – and sometimes steeply – as a function of time.

The aim of the paper is first to present experimental results showing this phenomenon which we named “spontaneous ionic purification phenomenon” (SIP). In the text we also use the already known abbreviation EIS coming from the French name of the phenomenon. We give here some material for characterization and we assume that the phenomenon is due to the absorption of ions at the interfaces of the liquid with the metal. Then, the consequences

on the conductivity measurements are discussed, especially concerning the temperature dependence and the characterization of aged transformer oils.

2. Experimental

Measurements were performed using an IRLAB LDTR-2 instrument based on the alternate square wave method [2]. Conductance values as low as 2×10^{-14} S can be measured with an error of less than 1%. The test cells include two coaxial cylindrical electrodes made of stainless steel, each of them being insulated from the ground. We used the CL-1 model, with an electrode gap of 3.5 mm, and the CL-1a model, with an electrode gap of 1 mm. Both test cells have the same geometrical constant $k = 2.4$ m, defined by $\rho = k/G$, ρ being the resistivity and G being the conductance. Unless otherwise stated the CL-1a test cell was used. Before any measurement the test cells were carefully washed by ultrasonic cleaning in the presence of ethanol, and then they were dried at 110 °C for several hours. After such a process the test cells will be said to be “clean”.

The temperature was either room temperature – which lay between 18 °C and 24 °C – or 90 °C. The time duration to reach 90 °C from 20 °C was about 45 min. Unless otherwise stated, data are given for room temperature.

The samples had been taken on power transformers in service according to a strictly controlled procedure. They were kept in new aluminum bottles and we checked that, under these conditions, their resistivity remained a constant for at least 3 months.

* Corresponding author. IRLAB, 12 rue André Rivoire, 38100 Grenoble, France.
E-mail address: jean-cesar.filippini@grenoble.cnrs.fr (J.C. Filippini).

The instrument used allowed us to take the first measurement less than 1 min after test cell filling. This value will be considered as giving the resistivity reference of the liquid, in accordance with the new IEC 61620 Standard [3]. Then the instrument continuously recorded the time-dependence of the conductance and of the temperature.

3. Results and discussion

The measurements presented hereafter were performed on seven samples of mineral oils taken from transformers in service for more than 10 years – references U1–U7 – and new oil, N1. The references of the oils and the values of their resistivity measured at 20 °C are given in Table 1.

3.1. The observed phenomena

Fig. 1 gives the time-dependence of the test cell conductance – given here in reduced coordinates, the reduced conductance being 1 at initial time – for two oils of very different behaviours: the conductivity of the oil U7 is practically a constant whereas that of oil U1 is clearly decreasing with time. The decrease, initially sharp, progressively reduces. All the oils taken from transformers – except U6 and U7 – exhibit this behaviour.

The phenomenon is more or less marked according to the oils. Fig. 2 gives some examples of the conductivity decrease during the first hours after test cell filling. For oil U1, the curve refers to a second filling of the same test cell a week after: we can see that the decrease kinetics is a little different.

3.2. Some features

The first question which occurred was the following: is the conductance decrease due to an evolution of the liquid itself – by a decrease of the volumic charge density – or to an evolution of the properties of the electrodes which would progressively limit the current flow? A simple experiment showed that the phenomenon is really related to a decrease of the charge density in the liquid, although a possible alteration of the electrodes cannot be excluded: if the liquid remained in a test cell for a long time is poured into a clean one, the initial conductivity value measured in the new test cell is found to be the same as the final resistivity in the first test cell.

These observations recall another phenomenon, known for a century and called “electrical purification” of liquids. When an insulating liquid is submitted to a step of voltage, the long term current – i.e. much beyond the transit time of ions between the electrodes – can decrease with time. Moreover it was shown by experiments – formerly performed in our laboratory – on polar liquids in a closed circuit including a pump, a d.c. voltage test cell and a control test cell that the charge volumic density in the liquid could decrease after a long application of the d.c. voltage.

Another question arose: in our experiments the measuring voltage – an alternate square wave of 10 V – was permanently

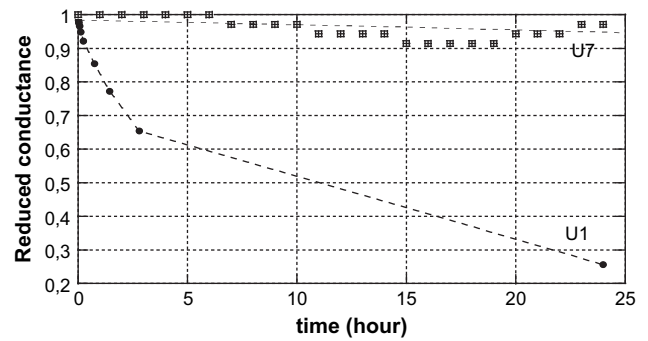


Fig. 1. The time-dependence of the conductivity of oils U1 and U7 at room temperature (CL-1a test cell).

applied: was the phenomenon connected with the application of the voltage as it is the case for electrical purification? Two experiments in two identical test cells, one of them being under voltage and the other without voltage, gave the same result, thus showing that the applied voltage does not play a role in the observed phenomenon. We concluded that the liquid becomes more insulating by its sole presence in the test cell; for this reason, we called the phenomenon spontaneous ionic purification (EIS).

It is reasonable to say that this decrease of charge density takes place because the ions and the molecules in equilibrium with them leave the liquid through the available interfaces: free surface, by evaporation, contact with metals or by adsorption. It seems improbable that a selective evaporation of dissociable chemical species takes place but there is no experimental evidence for it. The role played by the walls of the test cell, however, seems much more likely and we present here two experiments supporting this assumption.

In the first experiment we compare the results obtained using two test cells of same geometrical constant k but differing by their electrode gap d and by their χ constant, a parameter measuring the ratio between the total area of the walls and the volume of the liquid contained in the cell [4]. Fig. 3 shows the decrease of the conductance of the two test cells filled with oil U1. The decrease is much more marked in the CL-1a cell which presents the highest χ (7.9 cm^{-1} instead of 2.9 cm^{-1} for the CL-1 cell). If the EIS phenomenon comes from interface mechanisms between the liquid and the walls of the test cells we understand that the conductance decrease is the fastest in the CL-1a test cell where the influence of the walls is the largest.

In the second experiment we modify the nature of the electrode metal. We made a new test cell identical to CL-1a model but with

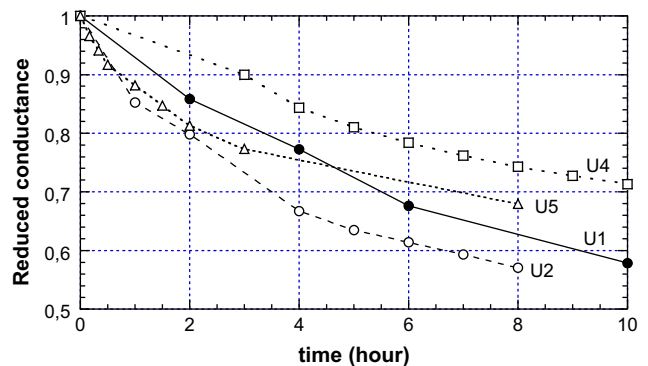


Fig. 2. The time-dependence of the conductivity of oils U1, U2, U4 and U5 at room temperature (CL-1a test cell).

Table 1
The reference and resistivity ρ of studied oils.

Oil	U1	U2	U3	U4	U5	U6	U7	N1
Reference	Univolt 54 (U54)	U54 Esso	Diala F Shell	U54 Esso	U54 Esso	U64 puis U54 Esso	Diala S Shell	U54 Esso
$\rho \times 10^{-12}$ ($\Omega \text{ m}$)	3.2	31	4.1	20	3.0	2.5	7.5	110

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