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Extraction of low molecular weight acids from transformer liquids using water extraction technique

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Abstract- Acidity has been recognised to be an excellent marker of the transformer insulation system. In the recent decade, a subgroup of the acids, known as low molecular weight acids (LMA), have been identified to be the cause of acid catalysed degradation of the paper insulation. Due to the unavailability of a standard method, LMA in transformer oil is commonly measured through a water-extraction process where LMA is extracted into water prior to the titration. This contribution investigates the effects of some key parameters of the extraction process including stirring speed, stirring duration and the separation period. Experiments are conducted with two types of transformer liquids including a mineral oil and a synthetic ester. Results indicate that the best extraction efficiency for the transformer liquids can be reached at a stirring speed of 650 rpm. Furthermore, it is found that the LMA extraction is completed within 1 hour and 3 hours of stirring for the mineral oil and the synthetic ester, respectively. The mineral oil had higher LMA extracted in water than the synthetic ester in a wide range of initial acidity concentration. This is due to a residual amount of LMA remaining in the ester liquid irrespective of the initial acidity.

I. INTRODUCTION

Extensive studies on the UK transformer population have found that around 50% of the transformers are reaching 50 years of operating time, which is beyond their design life [1]. To avoid failure of these expensive and important assets, information on their conditions are collected through chemical ageing markers in transformer liquid, which allows network operators to plan for timely maintenance and replacement.

A transformer's insulation system comprises of paper insulation immersed in insulating liquid (commonly mineral oil) to protect the windings from short-circuit failures. Paper insulation cannot be removed during operation unlike transformer insulating liquids and additionally its degradation mechanism is an irreversible reaction. As a consequence, a transformer's health condition is closely linked to the condition of the paper insulation.

Transformer insulation paper is mainly made from softwood Kraft pulp and its constituents are: cellulose, hemi-cellulose and lignin. Paper degradation occurs through oxidation, hydrolysis and pyrolysis where the insulation is exposed to chemical, physical or thermal stresses for long periods of time [2]. These reactions will lead to the production of different molecular by-products (such as CO, CO₂, furfural compounds and methanol), which can be used to monitor the condition of the paper insulation [3]. Degradation of transformer insulation initiates with the oxidation of transformer liquid and paper due

to their lower activation energy and the abundance of oxygen at the initial stage of a transformer's operating life [4]. These reactions produce acids that dissociate to form hydronium ions. The generation of acidic by-products slowly suppresses the oxidation reactions and promotes hydrolysis leading to the production of more water and acids. The processes can thus be regarded as an acid catalysed autocatalytic reaction [4].

Acidic by-products are one of the core molecular groups involved in the molecular interactions during the lifetime of a transformer [4]. Not surprisingly, it is recognised as a prominent chemical marker for transformer liquid and a potential marker for paper insulation [4, 5]. Acids produced during the ageing process can be further categorized as low molecular weight acids (LMA) and high molecular weight acids (HMA), both of which are carboxylic acids [6]. The contribution of these different types of acids to the ageing process of paper insulation is different. LMA have been found to be more active in the degradation of paper insulation. LMA are mainly generated from the chemical hydrolytic processes in the paper and due to their polar and hydrophilic nature they tend to accumulate in the paper insulation [6, 7]. Additionally, because the molecules are small they will also partition into the transformer liquid. Other factors that affect partitioning are: partial concentrations, polarity and temperature. LMA that are assumed to originate from the paper insulation ageing have a molar mass that ranges from 46 to 116 g · mol⁻¹. HMA have much larger molar masses that are typically greater than 240 g · mol⁻¹ [6]. HMA have been found to be generated mainly from chemical oxidation processes relating to the transformer liquid and due to their non-polarity and large molecular size they tend to stay in the transformer liquid [8]. Therefore, they have a negligible effect on paper degradation. However, as explained in [6], the current methods of measuring acidity in transformer liquid is in its infancy, and is limited as it can only measure total acid number rather than specifically the more detrimental LMA. In order to investigate LMA in the ageing process of paper insulation they need to be accurately and reliably separated from the other acids in transformer liquid. There is no standard measurement method for the extraction process of LMA. Commonly seen methods involve using water to extract LMA due to their polar hydrophilicity and solubility in water [6, 8]. Percentage extracted of LMA from transformer liquid could depend on different parameters of the extraction process. In this paper, the effects of stirring speed, stirring duration and acidity concentration on the extraction of

LMA from transformer liquid using water will be investigated for two types of transformer liquids including a mineral oil and a synthetic ester.

II. EXPERIMENTAL DESCRIPTION

A Test Objects

In the experiment two types of transformer liquids were investigated: Nytro Gemini X (inhibited mineral oil) and MIDEL 7131 (synthetic ester). The transformer liquids were filtered using a nylon membrane of pore size 0.2 μm and then degassed under vacuum at 85 $^{\circ}\text{C}$ for 24 hours for the mineral oil and 72 hours for the ester. Formic acid of >98% purity from Sigma Aldrich was used as a representative of the carboxylic acids belonging to LMA.

B Determination of Formic Acid Concentration and Acidity Number

Formic acids of masses ranging from 0.02 to 1 g were injected using a 500 μl SGE gas tight syringe (Sigma Aldrich) into 200 ml, 500 ml and 1000 ml of transformer liquids and the acidity was measured using potentiometric dynamic endpoint titrations according to IEC 62021-1 and IEC 62021-3, for mineral oils and synthetic esters respectively. A Metrohm 848 Titrino Plus with a Solvotrode easyClean glass electrode was used for the titration. The results are plotted in Fig. 1.

From Fig. 1 it can be seen that there is an approximate linear relationship between the acid added and the measured acidity for all investigated liquids. The figure shows how much acid needs to be added to get a particular acidity, which was used to control initial acidity concentration of the transformer liquids.

C Sample Preparation

Two 500 ml bottles with each type of transformer liquid were placed at room temperature and then injected with the appropriate mass of formic acid using the 500 μl gas tight syringe according to Fig. 1. Acidity of approximately 0.1, 0.3 and 0.5 mg KOH/g Oil, were prepared for each type of transformer liquid. The samples were then left to mix on a magnetic stirrer overnight (12 hours). The final acidity values obtained for each transformer liquid type are shown in Table 1.

Table 1 Controlled Initial Acidity Concentrations of Transformer Liquids

Liquid Type	Acidity in New Liquid (mg KOH/g Oil)	Controlled Acidity (mg KOH/g Oil)		
		0.10	0.34	0.51
Gemini X	<0.01	0.10	0.34	0.51
MIDEL 7131	<0.03	0.11	0.31	0.50

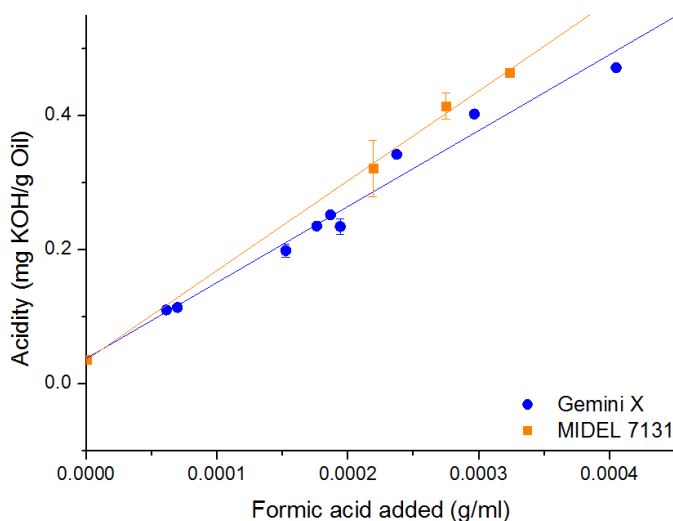


Fig. 1 – Concentration of added formic acid plotted against averaged acidity.

D Measurement of LMA in Transformer Liquid Samples

LMA in transformer liquid was measured through the procedure shown in Fig. 2 and the parameters shown in the reference method of Table 2. 25 ml of analytical grade water was added into 25 ml of transformer liquid. They were mixed on a magnetic stirrer for three hours and then left to separate for three hours into two distinctive layers. The two phases were then separated and the acidity was measured.

Effects of the stirring speed, stirring duration and the separation time on the LMA extraction process from the two transformer liquids were investigated individually while maintaining other parameters as in the reference method.

Table 2 – Parameters for the Acidity Separation Process

Controlled Parameters	Reference method	Variations
Transformer liquid (ml)	25	-
Water (ml)	25	-
Stirring Speed (rpm)	650	300, 650 and 1000
Stirring Duration (hours)	3	1, 3, 5, 7 and 12
Separation Time (hours)	3	0.25, 0.5, 1 and 3
Temperature ($^{\circ}\text{C}$)	20	-

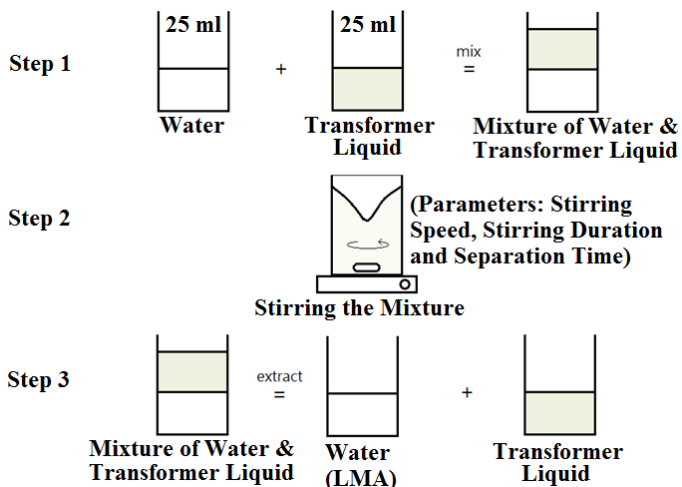


Fig. 2 – Water extraction technique to separate LMA from transformer liquids

III. RESULTS & DISCUSSION

A Effect of Stirring Speed on LMA Percentage Extracted

Fig. 3 shows a plot of percentage extracted against stirring speed for an initial acidity of 0.5 mg KOH/g Oil in two transformer liquids. Percentage extracted is calculated by (1).

$$\eta = \left[\frac{A_2}{A_1} \right] \times 100\% \quad (1)$$

Where η is the percentage extracted (%), A_1 is the initial acidity controlled in the transformer liquid and A_2 is the acidity of the extracted LMA in the water.

From Fig. 3, an optimum stirring speed of 650 rpm was observed in terms of percentage extracted for Gemini X. A decrease in the percentage extracted was seen at both 300 and 1000 rpm. This could have occurred due to a slower rate of diffusion at lower stirring speeds and evaporation of formic acid at higher stirring speeds as a result of its volatility. For MIDEI 7131, there is a negligible change in the percentage extracted of LMA as the stirring speed increases from 300 to 1000 rpm. This phenomenon might be a result of MIDEI 7131 being a more polar molecule and mixing well with the water during the 3-hour stirring period. Experiments conducted using transformer liquid samples with an acidity of 0.1 and 0.3 mg KOH/g Oil also indicated a similar optimum stirring speed.

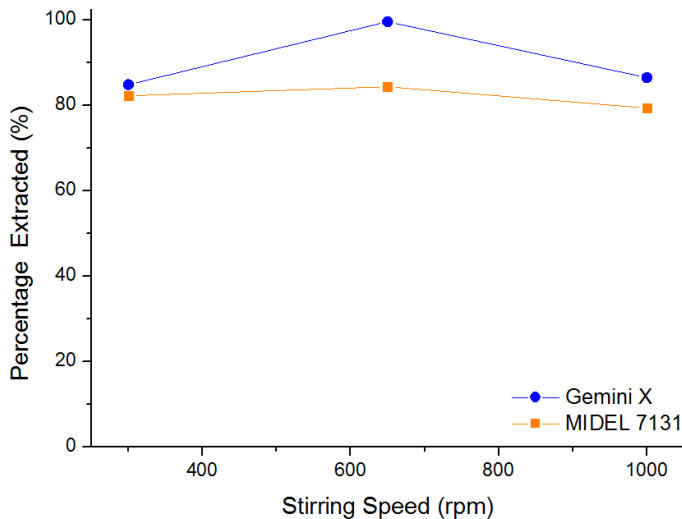


Fig. 3 - Percentage extracted against the stirring speed for Gemini X and MIDEI 7131 with an initial acidity of 0.5 mg KOH/g Oil

B Effect of Stirring Duration on LMA Extraction

Fig. 4 shows the effect of stirring duration on the LMA extraction process. Experiment was conducted at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil. The stirring duration of the samples was varied from 1 to 12 hours. The results show that for the mineral oil the extraction process is completed within the first hour, whereas for the synthetic ester this takes approximately upto three hours. The short period of time for extraction in the mineral oil is most likely due to its non-polar nature. The polar LMA molecules are more likely to diffuse into water rather than staying in oil. For MIDEI 7131 the

attraction between LMA and ester can be stronger due to their polar nature, which is probably why it takes longer for LMA to be extracted into water from the synthetic ester. In addition, a residual amount of LMA was found in MIDEI 7131 even after 12 hours of stirring. This means that there will be a small amount of LMA than cannot be separated using water, which is trapped by the polar synthetic ester molecules via hydrogen bonding.

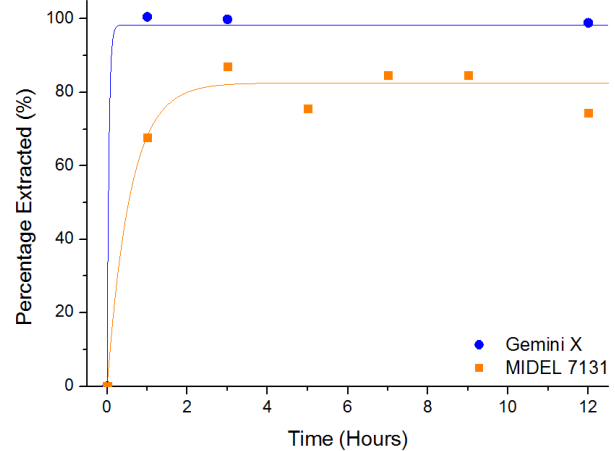


Fig. 4 – Acidity against time for Gemini X and MIDEI 7131 stirred at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil

C Effect of Separation Time on LMA Extraction

Even though the 3 hours of stirring together with 3 hours of separation time is sufficient, laboratories are interested in faster measurement procedures. Hence, the effect of separation time was investigated to determine the possibility of shortening the measurement duration. Transformer liquid samples prepared with 0.5 mg KOH/g oil acidity were stirred at 650 rpm for 3 hours and left to separate for different durations from 0.25 to 3 hours. Fig. 5 shows the acidity in water at different separation times. It can be seen that the acidity is constant and does not change as separation time changes from 0.25 to 3 hours for the two types of transformer liquids. This suggests that LMA has diffused into the water during the stirring period the separation time could be reduced to 0.25 hour (15 minutes) if desired.

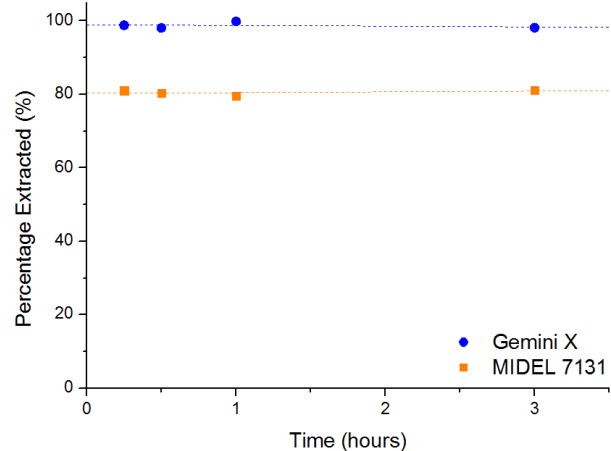


Fig. 5 – Acidity of water against separation time for Gemini X and MIDEI 7131 stirred at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil

D Effect of Initial Concentration on Extraction of LMA

Fig. 6 shows the amount of extracted acids in water against the injected acidity in transformer liquid measured at three different initial acidity levels, which used the reference method in Table 2. For the investigated acidity range, the results show that close to 90% or more of LMA can be extracted from the mineral oil.

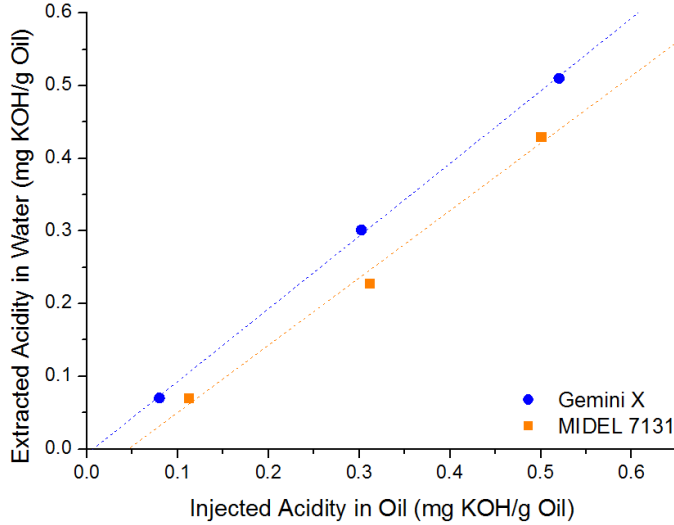


Fig. 6 – Deviation of extracted Acidity for Gemini X and MIDEL 7131

However, for synthetic ester, extraction was lower than the mineral oil. This was a result of the residual LMA, which is higher in ester liquids due to their increased polarity. From the experiments the residual amount for synthetic ester was seen to be approximately 0.042 mg KOH/g Oil, and as can be seen from the line fitting intercept on the x axis of Fig. 6. The residual amount of Gemini X is much lower and close to 0.007 mg KOH/g Oil.

For example, Fig. 6 could be used as a calibration curve to calculate the LMA (Formic acid) in the actual samples of transformer liquids within this study from their LMA measurements in water. Two equations are obtained; one for Gemini X, and one for MIDEL 7131, (2) and (3) respectively.

$$A_{Gi} = 0.007 + A_{GW} \quad (2)$$

$$A_{Mi} = 0.042 + 0.927A_{MW} \quad (3)$$

Where A_{GW} is the acidity, in mg KOH/g Oil, of LMA extracted from Gemini X; A_{MW} is the acidity, in mg KOH/g Oil, of LMA extracted from MIDEL 7131; A_{Gi} is the initial acidity in Gemini X. A_{Mi} is the initial acidity in MIDEL 7131.

The anticipated outcome is that a method has been developed whereby LMA (which are more polar and hence more soluble in water and paper) are preferentially removed from oil by water whereas HMA are less polar and tend to stay in the transformer liquid. The types of acid that are more soluble to water (and paper) are therefore more likely to be detrimental to paper and hence transformer lifetime. Therefore this method can provide greater understanding of acidity number.

IV. CONCLUSION

A water extraction technique for LMA in a mineral oil and a synthetic ester was investigated. The effects of the following parameters: stirring speed, stirring duration, liquid type, acidity concentration, and separation period were studied. A reference method was optimised at the room temperature whereby samples are stirred at 650 rpm; stirred for a duration of 1 hour for mineral oils and 3 hours for synthetic esters; and then left to separate for 30 minutes.

It was also found that the ultimate extraction of acid in the synthetic ester will always be less than that in the mineral oil at the same initial LMA concentration due to its polar chemical nature. A residual of acids was also noticed during the extraction of LMA from the synthetic ester. It was noticed from the experiments to be approximately 0.042 mg KOH/g Oil. However, the study needs to extend to other types of LMA.

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