# ACID GENERATION STUDY OF NATURAL ESTER

N. Azis and Z. D. Wang*
The University of Manchester, Manchester M60 1QD, UK
*Email: zhongdong.wang@manchester.ac.uk

**Abstract**: Acids are known as one of the ageing by-products of insulating paper and oil in transformers. Acids for mineral oil-paper combination consist of Low Molecular Weight Acids (LMA) and High Molecular Weight Acids (HMA). Few studies have been carried out on the generation of LMA and HMA in natural ester, thus further investigation on these parameters is needed. The study focuses on measuring the Total Acid Number (TAN), LMA and HMA generation in natural ester-paper combination at open and sealed condition under high temperature ageing. It is found that paper in natural ester contains less amount of LMA compared to that in mineral oil and most of the acids in natural ester are HMA.

## 1 INTRODUCTION

In recent years, application of alternative insulating liquids for transformers is becoming an important topic since the demand for the high fire safety is increased. Natural ester is viewed as one of the possible replacement for mineral oil.

Acids are known to accelerate the ageing process of oil and paper. Recently it was suggested that current measurement technique of acidity is unsatisfactory since it could not distinguish the types of acids in oil [1, 2]. According to these studies, it was observed that acids generated from ageing of paper and mineral oil consists of LMA and HMA where LMA was found to be more dangerous since it could accelerate the paper degradation [2].

On the other hand, natural ester was shown to generate much higher acids than mineral oil and these acids could help to protect the paper through transesterification process [3]. However, there is no study being conducted on examination of the LMA and HMA of natural ester and its impact toward paper ageing.

The main aim for this paper is to understand the mechanism of TAN, LMA and HMA generation in natural ester and its effect toward paper ageing. High temperature ageing was performed under open and sealed conditions with common materials used inside a transformer which include paper, insulating liquid, copper and steel. Measurement of TAN, LMA and HMA was conducted for oil samples and LMA for paper samples. Tensile strength for each paper samples was also measured in order to study the effect of LMA and HMA on the paper ageing. This work was carried out with the motivation to update the knowledge of natural ester ageing especially on acids composition and generation.

## 2 AGEING OF NATURAL ESTER AND PAPER

### 2.1 Ageing of natural ester

Natural ester originated from glycerol and fatty acids which are known as trglyceride. Figure 1 shows the typical structure of the trglyceride molecule where the (R, R′, R″) groups consist of C8-C22 chains [4].

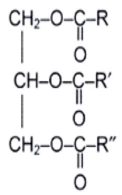
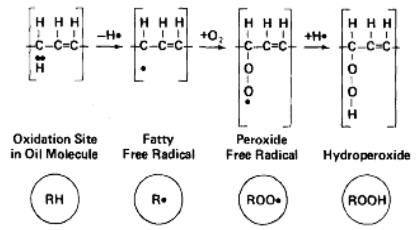


**Figure 1:** Structure of trglyceride [4]

#### *2.1.1 Oxidation and hydrolysis of natural ester*

Oxidation of natural ester can be described as ‘free radical mechanism’ as seen in Figure 2a) [5]. The process starts when the hydrogen leaves α-methylenic carbon in the trglyceride molecule. This will cause the R• in the α-methylenic carbon becoming unstable and susceptible to oxygen attack. Once the R• reacts with oxygen, it will create peroxide free radical and promotes further oxidation. The final stage of oxidation is the formation of hydroperoxide where the decomposition of this product will creates aldehydes, ketones, alcohols and fatty acids. There are several factors that can affect the oxidation process of natural ester such as enzymes, metals, temperature and aeration [5]:




a) Oxidation of natural ester [5]

$$C_3H_8(OOCR)_3 + H_2O \Leftrightarrow C_3H_8(OH)(OOCR)_2 + R\text{-}COOH$$
(triglyceride + water ⇔ diglyceride + fatty acid)

$$C_3H_8(OH)(OOCR)_2 + H_2O \Leftrightarrow C_3H_8(OH)_2(OOCR) + R\text{-}COOH$$
(diglyceride + water ⇔ monoglyceride + fatty acid)

$$C_3H_8(OH)_2(OOCR) + H_2O \Leftrightarrow C_3H_8(OH)_3 + R\text{-}COOH$$
(monoglyceride + water ⇔ glycerol + fatty acid)

b) Hydrolysis of natural ester [6]

**Figure 2:** Oxidation and hydrolysis mechanisms of natural ester

Hydrolysis of natural ester can take place in three stages where all of them are reversible which can be seen in Figure 2b) [6]. The first stage is the creation of diglyceride formed by trglyceride interaction with water. Once the diglyceride reacts with water, it will create monoglyceride which will form into glycerol as final reaction product. During all stages, fatty acid will be created as a by-product result.

## 2.2 Ageing of paper

Paper is well known as one of the basic insulation material in a transformer. The main constituent of paper is cellulose that consists of anhydro β-D glucopyranose units linked to each other as shown in Figure 3. The repeating units of glucose ring in the structure bind together by the glycosidic bond which is one of the parameters that contributed to the paper strength [7]. This glucose ring is connected together through the hydroxyl groups. According to previous studies, paper in the transformer mainly is subjected to two ageing mechanisms which are oxidation and hydrolysis [8, 9].

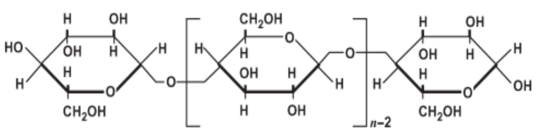


**Figure 3:** Anhydro β-D-glucopyranose monomer units

### *2.2.1 Oxidation and hydrolysis of paper*

Oxidation starts by attacking the hydroxyl group in cellulose structure and weakening the glycosidic bond. Carbonyl and carboxyl groups will be created as secondary ageing by-products which will promote further oxidation [7]. Once by-products such as water and acid are created, hydrolysis will be promoted and cause further degradation on the paper.

Hydrolysis is known as the main ageing mechanism of paper in transformers. Through hydrolysis, glycosidic bond will be scissioned and form free glucose rings [7]. Recently, it was found that hydrolysis of paper is catalyzed specifically by hydrogen ions originated from dissociated acids which could cause rapid depolymerization of paper [8].

# 3 EXPERIMENT DESCRIPTION

## 3.1 Ageing materials

High temperature laboratory accelerated ageing experiment was conducted using materials based on the given ratio in Table 1. The temperature was set at 170°C and only 6 samples were placed in the air circulating oven at any given time in order to obtain a good and even temperature distribution between each sample.

**Table 1:** Oil, paper, copper and steel ratio

| Oil (ml) | Paper (g) | Copper (cm²) | Steel (cm²) |
|---|---|---|---|
| 900 | 7.86 | 0.20 | 6.62 |

## 3.2 Pre-processing of ageing materials

Two types of oils were used for the ageing experiment which is natural ester, FR3 and mineral oil, GEMINI X. Kraft paper with a density of 0.93 g/cm² was used for all ageing samples. These materials were first pre-processed in order to remove moisture and particles which can affect the ageing. The paper was first dried in vacuum oven at 85°C for 24 hours. Alternatively, the oil was first filtered by nylon membrane filter with a pore size of 0.2μm and later dried in vacuum oven for 72 hours. The next step was to impregnate the dried paper with oil in a 1l of lime soda glass bottle for 24 hours at 85°C in a vacuum oven. The resulting moisture content for paper and oil after these procedures are less than 0.5% and 10ppm. On the other hand, copper and steel were de-coated by a sand paper in order to remove the surface oxidation layer. The copper and steel were included in the ageing bottle before the ageing experiment was started.

Open and sealed ageing experiments were conducted in our study where for sealed samples, PTFE screw cap with a gasket ring was used and the sealing tape was wrapped around the bottle neck in order to reduce the migration of oxygen from outside. Open and sealed samples were aged for 10, 20, 23 and 27 days. However for natural ester, 23 days sealed sample, it was not used for analysis since it was found that there is probably a sealing problem.

### 3.3 Acids measurement in oil and paper

The measurement of oil acidity was performed according to IEC 62021 [10] by Metrohm oil titrino plus. The measurement of LMA and HMA in oil and paper was done according to the method described in following sections [1].

#### 3.3.1 *LMA and HMA measurement in oil*

25ml of oil was mixed with an equal volume of water and mixed overnight using a magnetic stirrer. The next step was to leave the mixture sample still for at least half an hour in order to separate into two layers. Water and oil layer were then extracted and titrated according to IEC 62021 [10]. The acidity result obtained from water layer is defined as LMA while the oil layer as HMA. Acidity of clean water was measured and subtracted from the LMA in oil measurement. The acidity of the sample was calculated according to the weight of oil used for extraction.

#### 3.3.2 *LMA measurement in paper*

A known weight of paper, ranging from 0.5 to 1.0 g, was prepared and immersed in 25ml of water for 3 days without stirring. After the extraction period, 10ml of the extracting water was titrated according to IEC 62096 [11]. The leftover paper was dried in air circulating oven at 70°C for 2 day and acidity was calculated base on the dry weight of paper.

### 3.4 Tensile strength measurement of paper

As defined in IEC 1924, tensile strength is “the maximum tensile force per unit width that paper and board will withstand before breaking” [12]. Tensile index (TI) is much preferred to represent the mechanical strength since it could eliminate the influence of thickness. TI can be calculated as $TI = (F / w) / g$ (1):

$$TI = (F / w) / g \qquad (1)$$

Where TI = Tensile index, Nm/g

F = Failure load, N

w = Width, m

g = Grammage, g/m²

For each ageing duration, at least 8 samples were tested using INSTRON equipment since paper samples are quite limited. The crosshead speed was set to 20 mm/min. All measurements for paper samples were tested under 180mm gap length.

## 4 RESULTS AND DISCUSSIONS

### 4.1 Comparison between mineral oil and natural ester for sealed ageing experiment

A study was conducted on the partitioning of LMA and HMA in oil for natural ester and mineral oil as shown in Figure 4 and Figure 5. It can be seen that LMA is higher than HMA in mineral while HMA is higher than LMA in natural ester. It was also observed that the total acid is much higher in natural ester and hence the absolute amount of LMA in oil for natural ester is higher than mineral oil. This could well because that natural ester is much more polar and therefore the partition between paper and natural ester favours the stay of LMA in natural ester.

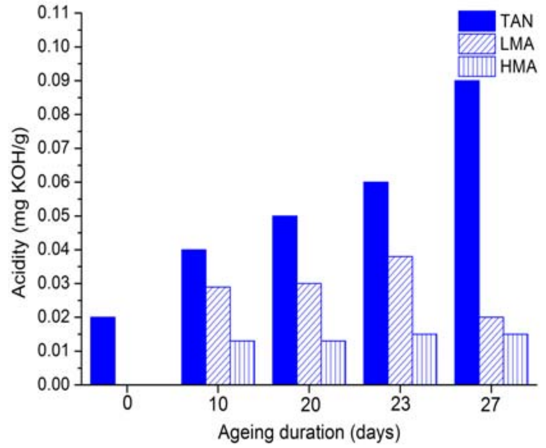



**Figure 4:** TAN, LMA and HMA in mineral oil (sealed)

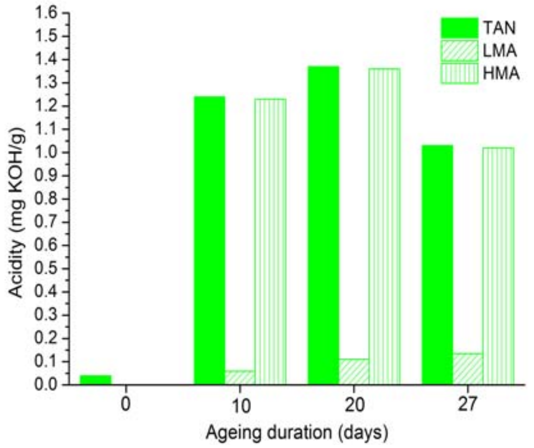



**Figure 5:** TAN, LMA and HMA in natural ester (sealed)

Table 2 shows percentage composition of LMA and HMA in mineral oil and natural ester. It was found that mineral oil has higher percentage of LMA than natural ester. Most of acids in mineral oil are LMA which percentages are ranging from 51.11% to 71.33%. On the other hand, natural ester has much lower LMA of the TAN than mineral oil ranging from 4.63% to 11.63%. It was found that most of acids in natural ester are HMA ranging from 88.28% to 95.37%. The reason for the high percentage of LMA in mineral oil is probably due to LMA migration from the paper. This phenomenon happens because the paper might be saturated by LMA which in turn force this acid to migrate into oil. This is supported by Figure 6 where LMA in paper for mineral oil is quite high and remains constant after 20 days of ageing.

**Table 2:** Percentage of LMA and HMA in oil for mineral oil and natural ester (sealed)

| Ageing time (days) | Mineral oil (%) | | Natural ester (%) | |
|---|---|---|---|---|
| | LMA | HMA | LMA | HMA |
| 10 | 68.40 | 31.60 | 4.63 | 95.37 |
| 20 | 70.35 | 29.65 | 7.53 | 92.47 |
| 23 | 71.33 | 28.67 | - | - |
| 27 | 51.11 | 48.89 | 11.72 | 88.28 |

It can be seen in Figure 6 that LMA in paper for mineral oil is higher than natural ester. The increment of LMA in paper for mineral oil is almost linear where the concentration starts to slightly declined after 23 days of ageing. On the other hand, LMA in paper for natural ester remains almost unchanged after 10 days of ageing at much lower value than mineral oil.

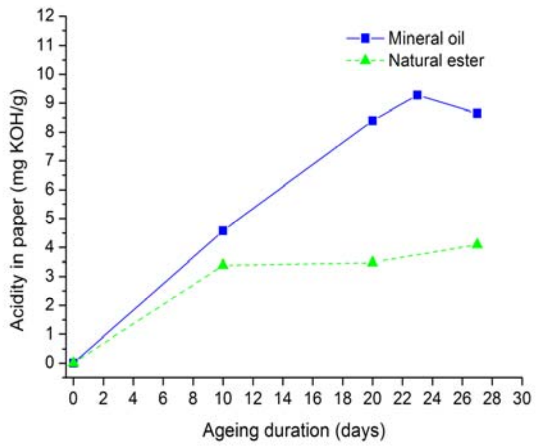



**Figure 6:** LMA in paper comparison between mineral oil and natural ester (sealed)

Figure 7 shows the TI comparison between ageing of paper and mineral oil/natural ester. It is believed that for these case studies, the ageing of paper in both mineral oil and natural ester is mainly dominated by both hydrolysis and pyrolysis since the system was sealed and high temperature was used for ageing. Paper aged in natural ester suffers rapid degradation from start of ageing and maintain at TI around 40Nm/g after 10 days of ageing. There is still some mechanical strength left in the paper at this point and fairly in a good condition. On the other hand, paper aged in mineral oil experiences more severe degradation than natural ester where the TI reduces up to 11Nm/g. At this instant, the paper has lost all the mechanical strength and quite brittle.

As proposed in [13], natural ester provides two modes of protection to the paper:

a) Water scavenging

Natural ester has higher water saturation level than to mineral oil which could help to remove the moisture from the paper. Furthermore, once natural ester hydrolysed, it will consume water and thus help to dry the paper.

b) Hydrolytic protection

The long fatty acids generated from the hydrolysis process of natural ester could help to stabilize OH group of the paper. This process is called transesterification where the paper is protected from further degradation.

Supposing these modes of protections are water scavenging and hydrolytic protection, the direct reason for the good performance of paper-natural ester system can be due to less LMA stays in paper throughout the ageing duration and most of them prefer to stay in natural ester since it is much more polar. According to previous study, most of LMA mainly stays in paper and it was shown that these acids could accelerate the paper degradation process based on mineral oil studies [2]. However, in natural ester, LMA measured in paper for natural ester is much lower than mineral oil as seen in Figure 6.

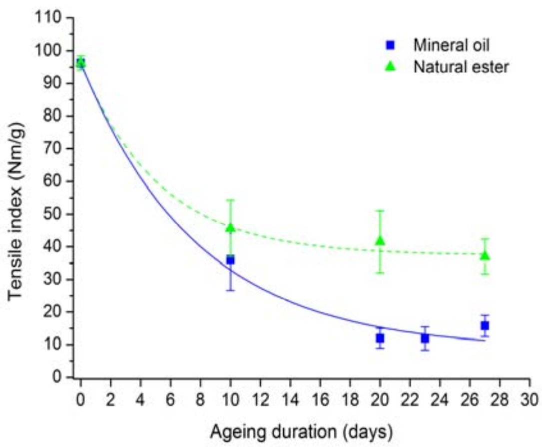



**Figure 7:** TI comparison between mineral oil and natural ester (sealed)

## 5 OXIDATION INHIBITOR DEPLETION PHENOMENON

A comparison was made between open and sealed ageing experiment for natural ester. It is suspected that for open samples, the ageing of paper-natural ester system is mainly dominated by oxidation and pyrolysis since the sample was subjected to high temperature and exposed to air. It can be observed in Figure 8 where open samples generate higher TAN than sealed samples. TAN for open samples shows a sudden jump after 10 days of ageing and it was followed by the physical change of the oil. The probable reason behind this phenomenon is due to the severe oxidation which causes the oxidation inhibitor to deplete. Once this event happens, the ageing of natural ester will be accelerate rapidly and cause acids to increase radically.

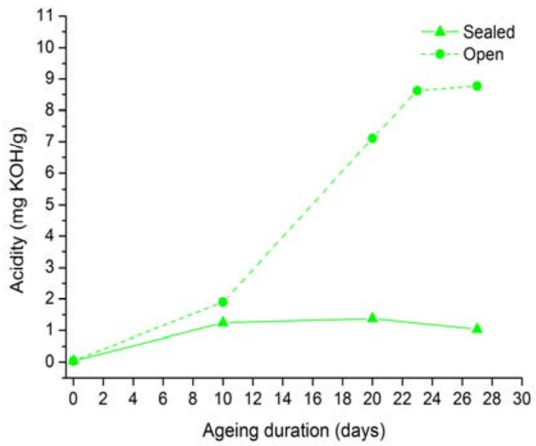



**Figure 8:** TAN comparison between sealed and open samples (natural ester)

The oil starts to gel and change to a dark colour after 10 days of ageing which can be seen in Figure 9a). LMA and HMA in oil for open samples could not be determined since the mixture of water and oil could not be separated and a yellowish solution was created as shown in Figure 9b). It is believed that the chemical structure of the natural ester has changed significantly after 10 days of ageing.

a) Open sample b) Mixture of oil and water

**Figure 9:** Natural ester conditions after 10 days of ageing (open)

## 6 CONCLUSIONS

Less LMA generated from ageing of paper and natural ester stays in paper than that of mineral oil for sealed ageing experiment, this could be the direct reason why there is less severe degradation to the paper in natural ester than in mineral oil, apart from water scavenging and hydrolytic protections.

Paper-mineral oil system generates quite high LMA which in turn might cause the paper saturated with these acids and hence the rest of them migrate into the oil, and this might be the reason for the high percentage of LMA in mineral oil. Furthermore, the high LMA concentration is one of the reasons for paper aged faster in mineral oil than in natural ester.

## 7 ACKNOWLEDGMENTS

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