Aging Properties of Monoesters and Comparison with Tri-ester and Mineral Oil

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Aging Properties of Monoesters and Comparison with Tri-ester and Mineral Oil

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Abstract—Two types of esters derived from vegetable oil, triglyceride (tri-ester) and monoester, have been implemented as insulation in the oil filled transformer. Tri-ester type is superior in flash point but inferior in viscosity and pour point compared to the monoester type. An accelerated aging test is an important test to assess a long time performance of an insulation system. Two kinds of monoesters, palm fatty acid ester (PFAE) and stearic/oleic/linoleic acids methyl esters (M182), and one tri-ester, Envirotemp (FR3), were thermally aged at the temperature of 120 °C for 60 days. The aging test was performed with the presence of a limited amount of air in oil sample by using as-received oil. The important properties like breakdown voltage, resistivity, and moisture content are evaluated at each 15 days interval. Experiment on mineral oil under the same condition was also conducted for comparison.

Keywords—aging; breakdown voltage; moisture content; natural ester; volume resistivity.

I Introduction

Natural esters of tri-ester type have been successfully implemented in distribution transformer during the last two decades and their implementation in power transformer is now rapidly growing [1]. In Japan, a chemical company Lion Corporation developed monoester type insulating oil, synthesized from palm oil, called palm fatty acid ester (PFAE) [2]. In comparison with other esters, the natural ester of tri-ester type and synthetic ester, PFAE has some advantages and disadvantages, as indicated in Table I [3]. The PFAE has the same levels of biodegradability as that of tri-ester and synthetic ester, which is superior to mineral oil, but the prices of all esters are also at the same levels, which is inferior to mineral oil. The naturalness of PFAE is comparable with tri-ester, and is better than synthetic ester, whereas its oxidation stability is comparable with synthetic ester, and is better than tri-ester. The viscosity of PFAE is 0.6 times less than mineral oil makes the cooling efficiency of the PFAE better than mineral oil and superior to tri-ester type insulating oil. However, PFAE is inferior in term of a flash point compared to the tri-ester type insulating oil, but still better than mineral oil [4].

An accelerated aging test is an important test to assess a long time performance of an insulation system. Ideally, the test is performed by incorporating all of the materials used in the real transformer. However, to get a better understanding of the role of each component in aging characteristics of combined material, it would be meaningful to assess the characteristic of oil aged alone. This is the motivation of the work reported in this paper. Aging properties of the monoester type insulating oil are compared with those of tri-ester type, as well as with mineral. The appearance of the oils is evaluated at each aging interval. The properties like moisture content, volume resistivity, and breakdown voltage are investigated and discussed.

TABLE I. Comparison of PFAE and other ester oils, relative to mineral oil.

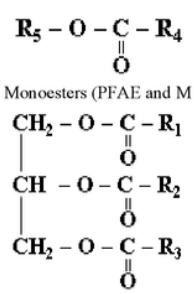
Property	PFAE	Tri-ester	Synthetic ester
Biodegradability	◎	◎	◎
Naturalness	◎	◎	○
Oxidation stability	◎	○	◎
Fire resistance	○	◎	◎
Cooling property	○	△	△
Price	△	△	△

◎ Superior to mineral oil,
○ Comparable to mineral oil
△ Inferior to mineral oil

II Experiment

2.1 Samples

Two kinds of monoesters, PFAE and M182, and one tri-ester, FR3 were used in the experiment. Chemical structures of monoester and tri-ester are shown Fig. 1. Mineral oil (MO) was also used for comparison. Some properties of tested oils are listed in Table II.



(a). Monoesters (PFAE and M182)

(b) Tri-ester (FR3)

Fig. 1 Chemical structure of natural esters; (a) Monoester, (b) Tri-ester.

TABLE I. Some properties of tested oils.

Properties	PFAE	M182	FR3	MO
Pour point, °C	-32.5	9.5	-21	-45
Flash point, °C	176	184	328	152
Kinetic viscosity (40 °C), mm²/s	5.06	4.6	33	8.13

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2.2 Experimental Procedures

2.2.1 Thermal Aging

Sample oil of about 4 kg was prepared for each oil type in a tightly sealed oil tank and aged in an oven at the temperature of 120 °C for 60 days. The photograph of the oil tank is shown in Fig. 2. The oil was used in the investigation without any pretreatment. Therefore, the oil sample still contained a limited amount of air (including oxygen) before being used in the aging test. Properties of oil such as appearance, moisture content, volume resistivity and breakdown voltage were evaluated at each 15 days interval. At each step of aging, a sample of about 1 kg for each oil type was taken out from the oil tank for properties measurement.

Fig. 2. The oil tank used for the thermal aging test.

2.2.2 Moisture Content Measurement

The moisture content of oil sample was measured using a moisture meter (CA-06, Mitsubishi Chemical Analytech, Japan), as shown in Fig. 3. The reported moisture content is the average of two measurement results.

Fig. 3. Moisture content measurement device.

2.2.3 Volume Resistivity Measurement

The volume resistivity (ρ) measurement was performed in accordance with JIS C 2101. The schematic test circuit and the test cell used for the measurement are depicted in Fig. 4. The detail measurement procedure can be found in [5].

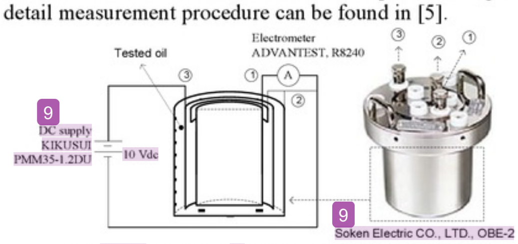

Fig. 4. The test circuit of volume resistivity measurement.

2.2.4 Breakdown Voltage Measurement

Breakdown voltage (BDV) measurement was conducted in accordance to JIS C2101, using the oil insulation tester (3811 IP-SSD, Musashi Corp. Japan), as shown in Fig. 5. It utilizes a test cell containing electrode pairs of sphere-sphere configuration. The diameter and the gap distance of sphere electrodes are 25 mm and 1 mm, respectively. The tester was set to the automatic operation mode with the rate of voltage rise of 3 kV/s.

Application of voltage was started at least 5 and 15 minutes after pouring the mineral and FR3 samples, respectively, into the test chamber. Standing times for PFAE and M182 follow that of mineral oil since the viscosity of both oils is lower than that of mineral oil. The measurements were conducted 6 times for each sample with a time delay between two consecutive measurements at least 2 minutes for mineral oil, PFAE, and M182 samples, and 6 minutes for FR3 sample. The delay time after a measurement is intended to allow breakdown products to disperse and gas to expel before the subsequent measurement was conducted so that the later measurement was not influenced by the previous one. The reported breakdown voltage is the average of twelve measurement results.

Fig. 5. Breakdown voltage measurement device.

III RESULTS AND DISCUSSION

3.1 Appearance

It appears that the color of all tested oils changes with aging time, as shown in Table III. PFAE, M182 and mineral oils which were initially transparent became yellow-green, light yellow and brown, respectively, at the end of aging, whereas FR3 was changed from light-green to dark-green. The most severe change was experienced by mineral oil, indicating the occurrence of oxidation in the oil.

TABLE II. THE CHANGE IN OILS COLOR AFTER AGING.

	PFAE	M182	FR3	Mineral Oil
Before aging				
After aging				

The oxidation of both mineral and natural ester oils could result in color change, but the occurrence of oxidation cannot be judged by the color change alone [6]. The formation of sludge in mineral oil, which is absence in other tested oils, provides additional evidence of the occurrence of oxidation in mineral oil. Other oxidation products of mineral oil are alcohol, water, aldehyde, and acid as in (1) – (11). The detail

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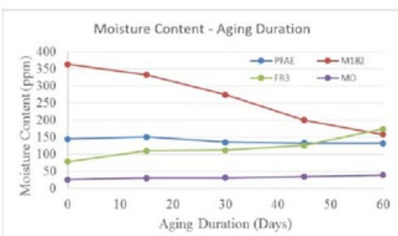
explanation of oxidation process of mineral oil can be found in [8].

$$RH \rightarrow R^* + H^* \quad (1)$$
$$R^* + O_2 \rightarrow ROO^* \quad (2)$$
$$ROO^* + H^* \rightarrow ROOH \quad (3)$$
$$ROOH \rightarrow RO^* + OH^* \quad (4)$$
$$RO^* + RH \rightarrow ROH + R^* \quad (5)$$
$$OH^* + RH \rightarrow H_2O + R^* \quad (6)$$
$$2ROO^* \rightarrow ROH + O_2 + RCOH \quad (7)$$
$$RCOH + O_2 \rightarrow RCOOOH \quad (8)$$
$$RCOOOH \rightarrow RCOO^* + OH^* \quad (9)$$
$$RCOO^* \rightarrow R^* + CO_2 \quad (10)$$
$$RCOO^* + RH \rightarrow R^* + RCOOH \quad (11)$$

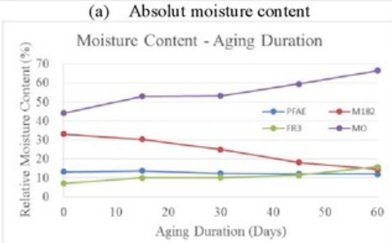
3.2 Moisture Content

Figs. 6a and 6b show the change in absolute and relative moisture contents, respectively, of all tested oils during the aging period. In term of absolute moisture content, mineral oil experiences the smallest change (Fig. 6a), but in term of relative moisture content, such change is larger than that of FR3 and PFAE, and comparable with that of M182, but with opposite directions (Fig. 6b). This is because mineral oil can only hold a very small amount of moisture compared to natural esters at the same temperature. The saturation limit of mineral oil at room temperature is about 60 ppm [9], whereas that of natural esters is about 1100 ppm (the saturation limit of FR3 is taken from [5]), whereas those of monoesters are approximated from [11]). Relative moisture content (M_{rel}) of oil is the ratio between absolute moisture content (M_{abs}) and moisture saturation limit of the oil (M_{SL}), based on (12) [6].

$$M_{rel} = M_{abs}/M_{SL} \quad (12)$$



(a) Absolut moisture content



(b) Relative moisture content

Fig. 6. The moisture contents of the oils as the function of aging duration.

It can be seen from Fig. 6 that relative moisture contents of mineral oil and FR3 increase during the aging period. The increase in moisture content of mineral oil supports the claim that the mineral oil was oxidized during the aging. Water is also known as one of the results of oxidized oil [6] [12].

Differing from previously mentioned oils, the relative moisture content of M182 and PFAE reduce significantly and slightly (Fig. 6). The reduction in moisture content of natural esters is attributed to the hydrolysis reaction, which consumes water and produces acids, based on (13). The initial moisture contents of M182 and PFAE were significantly and slightly high, 364 ppm or 33.1% and 145 ppm or 13.2%, respectively (Fig.6a), hence, hydrolysis was the preferable degradation mode for both oils. FR3, whose initial moisture content was very low (79 ppm or 7.2%), preferred to be oxidized.

$$RCOOR + H_2O \leftrightarrow RCOOH + ROH \quad (13)$$

The increase in acid values of PFAE and M182 (Fig. 7), measured by Potentiometric titration (COM-1700A, HIRANUMA SANYO Co.) in accordance with JIS C2101, and the reduction in their moisture contents (Fig. 6) confirm the occurrence of hydrolysis in both oils.

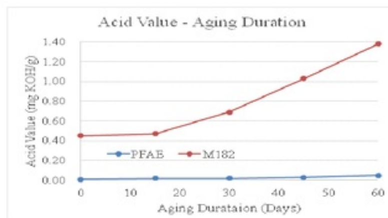


Fig.7. The acid values of PFAE and M182 as the function of aging duration.

3.3 Volume Resistivity

Fig. 8 shows volume resistivity of all tested oils as a function of aging duration. M182 and mineral oil exhibited the remarkable decrease in the volume resistivity during the first 15 days of aging, and their rates remain lower than those of PFAE and FR3 at the end of the aging period. These change, again, reflect the more severe degradation being experienced by both oils compared to PFAE and FR3 oils.

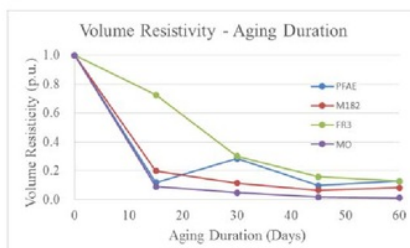


Fig. 8. Volume Resistivity of the oils as the function of aging duration.

The combination of higher concentrations of moisture and acids is suspected to be the factors responsible for the significant reduction in volume resistivity of the M182 oil. It should be noticed that the moisture content of M182 remained the highest among other oils until 45 aging days (Fig. 6a).The

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similar factors seem to contribute to the noticeable decrease in volume resistivity of mineral oil, but with the different mechanism. Mineral oil was oxidized, resulted in the productions of moisture (6) and acids (11). The relatively smaller change in the volume resistivity of PFAE and FR3 are attributed to the slight hydrolysis and oxidation, respectively. The very low volume resistivity of PFAE at 15 days of aging is thought to be a bias and caused by other unrecognized factors.

3.4 Breakdown Voltage

Fig. 9 shows the change in the breakdown voltage of all tested oils as a function of aging duration. The breakdown voltage of M182 increased significantly during the aging period. This is an expected result since the relative moisture content of M182 decreased from 33.1% to 14.5 % as a consequence of hydrolysis. The breakdown voltage of mineral oil, on the other side, decreased significantly. This is due to the increase in relative moisture of the oil from 44.2 % and 66.6 % as a consequence of oxidation. It is well recognized that clean oils can hold water in dissolved form up to 30 % without significantly affecting the breakdown voltage of oils, irrespective of the oil types [10].

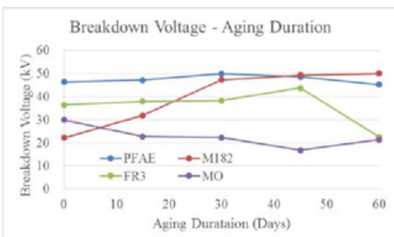

Fig. 9. The breakdown voltages of oils as the function of aging duration.

It is interesting that even though both M182 and mineral oils produce acids from the hydrolysis and oxidation, respectively, the effects on the breakdown voltage of, respectively, M182 and mineral oil are different. Acids do not affect the breakdown voltage of M182 oil but decrease the breakdown voltage of the mineral oil.

It can also be seen from Fig. 9 that the breakdown voltages of PFAE and FR3 relatively unchanged during the aging period. The breakdown voltage of PFAE is the highest among all tested oils until 30 days of aging and became comparable with that of M182 for the rest of aging duration, confirming a negligible effect of acids, produced from a slightly hydrolyzed PFAE and a slightly oxidized FR3, on the breakdown voltage of both oils. The presence of acids of low molecular weight (LMA) or of high molecular weight (HMA) with acidity up to 4 or 9 mg KOH/g, respectively, does not cause a significant decrease in the breakdown voltage of the natural ester oil [13]. The significant decrease in the breakdown voltage of FR3 at 60 days of aging is thought to be a bias and caused by other unrecognized factors.

IV CONCLUSIONS

Properties such appearance, moisture content, volume resistivity and breakdown voltage of thermally aged natural esters of monoester and triester types, as well as mineral oil, have been investigated. Some conclusions can be drawn as follows:

1. PFAE and M182 oils are slightly and severely hydrolyzed, respectively, which are indicated by the slight and remarkable decreases, respectively, in moisture content of both oils.
2. FR3 and mineral oils are slightly and severely oxidized, respectively, which is indicated by the increase in moisture content of both oils. The drastic change in color and formation of sludge in mineral oil indicate the severity of oxidation in the oil.
3. Acids produced by hydrolysis and oxidation contribute in decreasing volume resistivity of all oils but contribute in decreasing the breakdown voltage of only mineral oil.

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