Thermal Degradation Phenomena of Flame Resistance Insulating Paper and Oils

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ABSTRACT

In a search for mineral oil substitutes, we focus on silicone and ester oil. These insulating oils are fire-resistant and environmentally friendly. In previous studies, we investigated streaming electrification and dielectric breakdown phenomena in these new oils and found that their performance was similar to or better than that of mineral oil. In the present study, we focus on the thermal degradation of insulating oils. Thermal degradation tests in the presence of a solid insulator and copper carried out for 1000 h at 130 and 180 °C. Color changes, chemical analysis and dielectric breakdown characteristics were also investigated during thermal degradation of the insulating oils. We also investigated the mechanical strength of the solid insulator. The characteristics of aged oils were compared with those of fresh oils. Tested silicone oil presents better performance than esters and mechanical characteristics of paper remain unchanged in all resistance liquids.

Index Terms — **Silicone oil, Ester oil, Dielectric breakdown, Streaming electrification, Fresh oil, Aging oil, Thermal degradation, Nomex®, Chemical analysis.**

1 INTRODUCTION

MINERAL oils have high insulating and cooling performance, therefore they are used as an insulating medium in power transformers. However, the mineral oils, which are made from petroleum, are a dwindling resource and its flash point is very low. Therefore, we focused on the silicone and ester oils as mineral oil substitutes [1]. Silicone and ester oils are environmentally friendly, fire-resistant and abundant in resources. We previously investigated the dielectric breakdown, streaming electrification and burning characteristics of these oils [2]. The results revealed that most performance of silicone and ester oils were better than that of mineral oil. In the present study, we focus on thermal degradation. Insulating oils are operated with copper as conductive material and an insulator for a long time. And, copper wire and iron using in transformer at high temperature for a long time will be sulfured. Sulfide of copper and iron has an effect on insulating oil and paper of performance [3]. Therefore, investigation of degradation phenomena is important [4].

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Thermal degradation tests were carried out with a solid insulator and copper wire. Changes in oil color, chemical analysis and dielectric breakdown characteristics were investigated during thermal degradation. We also investigated the mechanical strength of the insulating paper and chemical analyses of fresh and aging oils.

2 TEST SAMPLES

Three insulating oils were used for thermal degradation experiments: dimethyl silicone oil (KF-96-20, Shinetsu Chemical), natural ester oil (Envirotemp FR-3®, Cooper Power Systems) and synthetic ester oil (Midel® 7131, M&I Materials). Table 1 lists their properties and Figure 1 shows their chemical structures [5-7]. Insulating oils were dehydrated under vacuum of ≤10 Pa at 130 °C for 6 h. The resulting oil had a moisture content of ≤10 ppm, which is similar to the level of power transformer operation [8]. The test insulator was made of heat-resistant aramid paper and pressboard (Nomex®, du Pont de Nemours & Co., USA). The insulating paper had dimensions of 203 mm×24.4 mm and was 0.075 mm thick, according to ASTM D-828. The pressboard had a diameter of 40 mm and was 5, 10 or 15 mm thick. The insulator was dried for at least 24 h in a furnace (atmospheric pressure, 130 °C) and it was

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assumed that the moisture content was ≤0.5% [9]. And, the amounts of oxygen contained in the oil were not measured. However, when making the adjustment for moisture of test oils, we were carried out vacuuming enough of test oil. Therefore, the amount of oxygen in oil is less. Copper wire of 0.7 mm in diameter was used as the electrical conduct. Copper wire was heated together with insulating oil and insulator (paper and press board) in a tank as an example. Silicone and ester oil did not generate sulfur in the insulating oil production process. Copper wire inside oil is not degraded by the sulfur content. Therefore, we did not investigate the copper wire.

Table 1. Properties of the insulating oils at 25 °C.

	Silicone oil	Natural ester oil	Synthetic ester oil	Mineral oil
Material	Silicon	Soybean	Synthetic	Petroleum
Specific gravity	0.95	0.92	0.97[a]	0.869[a]
Kinematic viscosity [mm^2/s]	20	34[b]	70[a]	7.75[b]
Flash point [°C]	260	316	260	148
Pour point [°C]	<–60	–21	–60	–32.5
Relative permittivity	2.7	3.2	3.2[a]	2.2

[a]Value at 20 °C; [b]value at 40 °C.

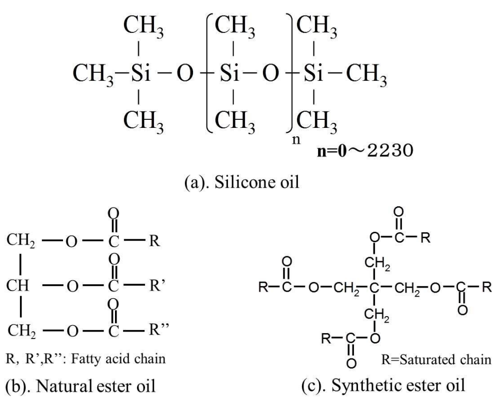

Figure 1. Chemical structure of test insulating oils

3 THERMAL DEGRADATION CHARACTERISTICS

Power transformer has been long time operation which is a composed insulation with insulating oil, paper and pressboard. Transformer arises thermal degradation when it is operating for a long time. This chapter reports the thermal degradation phenomena of insulating oils and papers.

3.1 AGING METHOD

The test materials had a mass ratio actually used in transformers [10, 11]. Table 2 lists the composition of the test materials. The test materials were measured by using weighing equipment. The materials were placed in a tank for heating. The tank was held at atmospheric pressure and was sealed with N_2 gas. Aging was carried out at temperatures of 130 °C and 180 °C (±10 °C) and different aging time was used to observe the insulating oils and paper. When the tank was initially opened, it was heated under vacuum. Then the pressure was returned to atmospheric pressure with N_2 gas and the next aging test was carried out.

Silicone and ester oils can be used at higher temperatures than that of mineral oil because of their better thermal class and flame resistance. Thus, transformer size can be reduced for the same load (as for mineral oil) or keep as it is with higher load.

Table 2. Ratio of test materials

Insulating oils	Oil quantity	Insulators	Copper wire
Silicone oil	5 L (4581 g)	157 g	132 g
Natural ester oil	5 L (4492 g)	152 g	128 g
Synthetic ester oil	5 L (4805 g)	163 g	137 g

4 CHANGES IN OIL COLOR

In this section we report on temporal response of insulating oils at each temperature. Especially, we focus on the thermal degradation of color change for insulating oils.

Figure2, 3 and 4 show color change for insulating oils heated at 130 °C and Figure 5, 6 and 7 show the color change of heating at 180 °C. Silicone oil does not change color so much at heating temperature at130 and 180 °C. On the other hand, natural ester oil and synthetic ester oil are changed color when heating temperature are 130 and 180 °C.

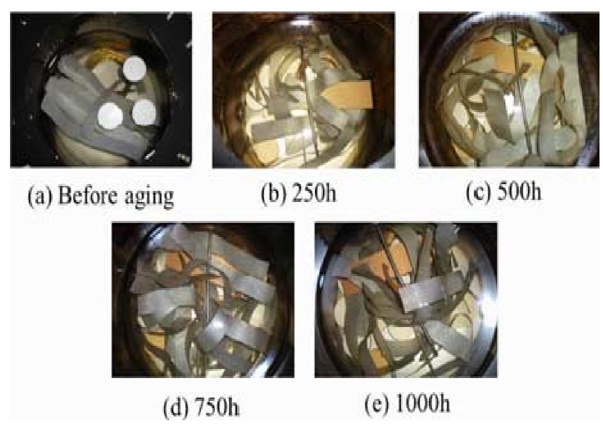

Figure 2. Temporal response of silicone oil (130 °C).

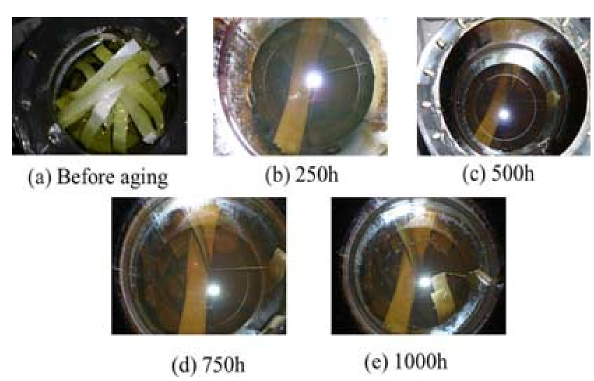

Figure 3. Temporal response of natural ester oil (130 °C).

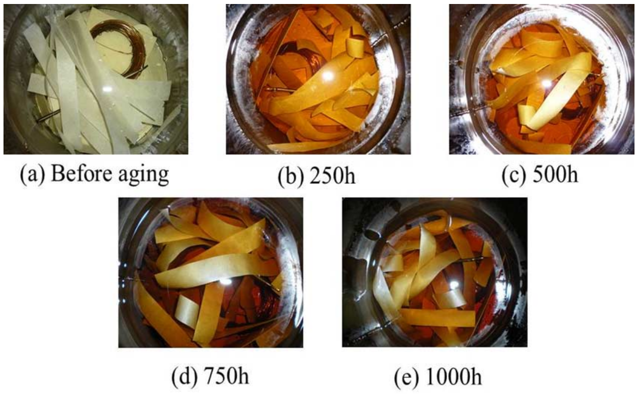

Figure 4. Temporal response of synthetic ester oil (130 ˚C).

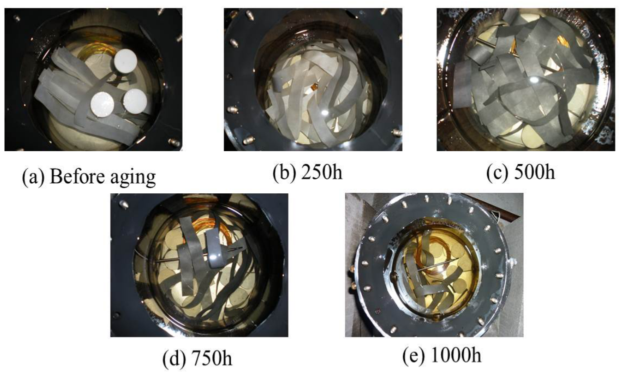

Figure 5. Temporal response of silicone oil (180 ˚C).

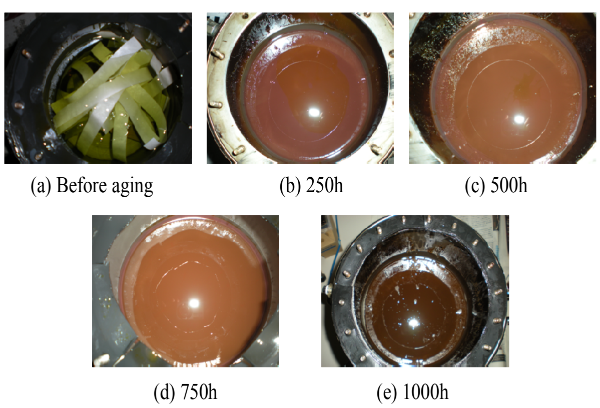

Figure 6. Temporal response of natural ester oil (180 ˚C).

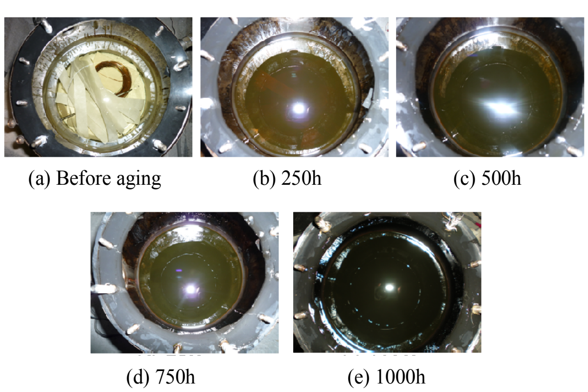

Figure 7. Temporal response of synthetic ester oil (180 ˚C)

Especially, natural ester oil and synthetic ester oil are changes in color at 180 °C. And so, we have possibilities changed the structure of the insulating oil by these reason. We report the chemical analysis of the fresh oil and aging oil in chapter 7.

5. DIELECTRIC BREAKDOWN VOLTAGE CHARACTERISTICS OF AGING OILS

In this chapter, we reported and compared the dielectric breakdown voltage characteristics of fresh and aging oils (180 ˚C, 1000 h) and temporal change in dielectric breakdown voltage characteristics (heating temperature is 130 ˚C).

5.1 EXPERIMENTAL METHOD

Insulating oils were tested before and after aging at 130 and 180 °C for 250, 500, 750 and 1000 h. An impulse voltage with a negative standard lightning waveform (–1.2/50 μs) was applied. We measured the BDV (Breakdown Voltage) by increasing the voltage in 5 kV steps from 60% of the expected BDV. Figure 8 shows the test model comprised hemispherical rod electrodes (gap length 2.5 mm). The tests temperature was 20±10 °C and tests were performed at least 10 times. However, the number of tests is more than 20 times when large variation in breakdown voltage value happened. When breakdown occurred, the material between the electrodes was stirred and next test was carried out.

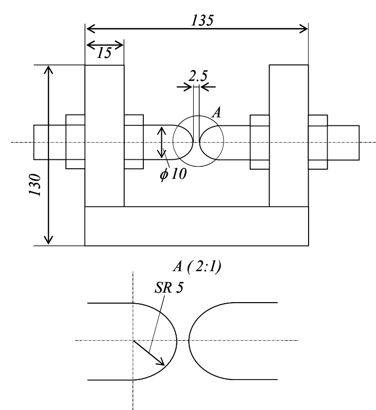

Figure 8. Test model.

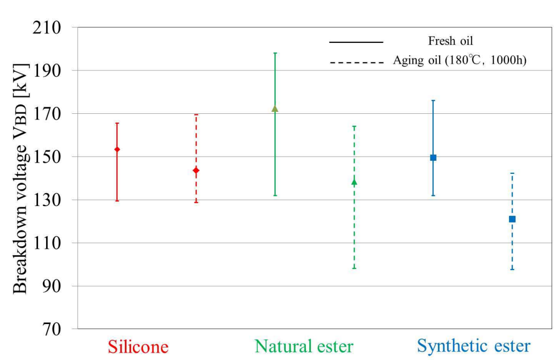

Figure 9. Dielectric breakdown voltage of various insulating oils. (Fresh oils and aging oils were heated for 1000 h at 180 ˚C)

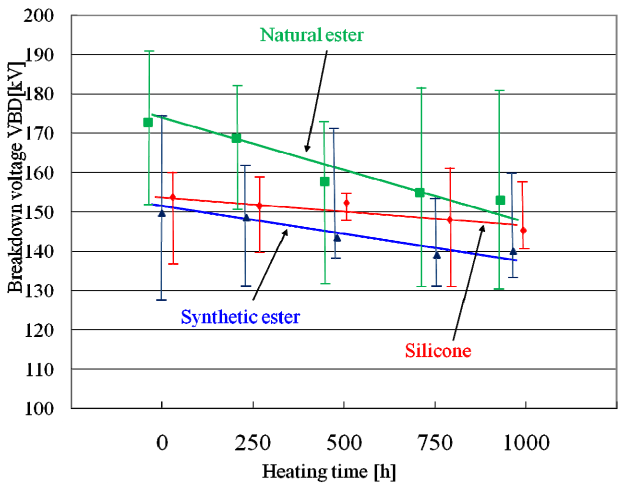

Figure 10. Temporal change in dielectric breakdown characteristics. (Heating temperature is 130 ℃).

5.2 EXPERIMENTAL RESULT

Figure 9 shows the breakdown characteristics of fresh and aged oils (180 °C). Figure 10 shows the temporal change in dielectric breakdown characteristics when heating temperate is 130 °C. The points are average value in using most concentrated points. The bars show the maximum and minimum value of breakdown voltage. From figure 9, the mean BDV was 149 kV for fresh synthetic ester oil. The mean BDV of aging oil was 121 kV for synthetic ester oil. The mean BDV was 153 kV for fresh silicone oil and 172 kV for natural ester oil. The mean BDV was 143 kV for aging silicone oil and 138 kV for natural ester oil. Therefore, after aging BDV decreased by 10% for silicone oil, 20% for synthetic ester oil, and 30% for natural ester oil.

Therefore, silicone oil has a small decreasing rate after aging breakdown voltage. And, silicone varied less in breakdown voltage value compared with ester oils. Performance of silicone is better than ester oils. Figure.10 shows the dielectric breakdown characteristics at each time when the heating temperature is 130 °C. The breakdown voltage was low in all of the insulating oils. Decreasing rate of BDV follow the order, silicone oil < synthetic ester oil < natural ester oil. As a result, silicone oil has the best performance as with heating temperature at 180 °C. We think about insulating oil of the decreasing rate of dielectric breakdown voltage in chapter 7.

6. TENSILE STRENGTH CHARACTERISTICS OF INSULATING PAPER

Transformer lifetime generally depends on the mechanical strength of the solid insulator [12]. Therefore, investigation of the insulator is necessary in order to determine the overall thermal deterioration characteristics. Therefore, the tensile strength of the aramid paper before and after aging was measured.

6.1 EXPRIMENTAL METHOD

Tensile strength tests on the Nomex® were carried out as described above after heating time of 0 (no heating), 250, 500, 750 and 1000 h at 180 °C. These tests were performed according to standard of ASTM D618 and D828 by DuPont Teijin Advanced Papers Limited. And, the tests were performed at least 6 times. But, when the Nomex® was heated at 1000 h by synthetic ester oil, the tests were measured 12 times. And, the points are average value.

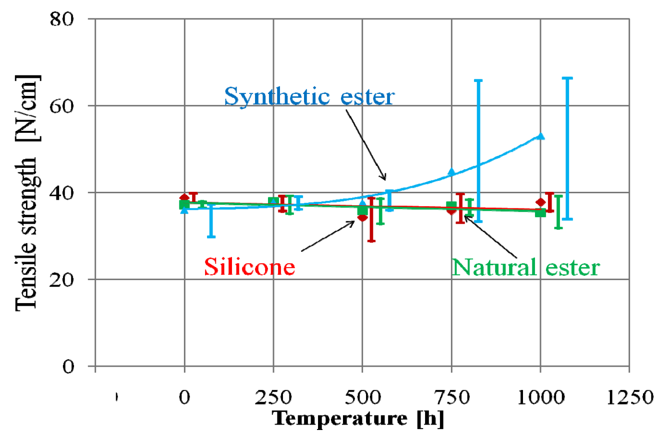

Figure 11. Tensile strange characteristics of Nomex® (180 ℃).

6.2 EXPRIMENTAL RESULT

Figure 11 shows the tensile test results. These can be summarized as follows. All insulating oils have varied value of tensile strength of insulating papers. When combining synthetic ester with Nomex® the tensile strength of insulating paper would increase at 750 and 1000 h. But, value of tensile strength of new insulating paper and after heating insulating paper are about the same. It is the reason that Nomex® can be used in this study because of its excellent heat resistance. So we can't confirm the degradation of tensile strength of insulating paper by thermal degradation. The composite of insulating system of Nomex® and flame-resistant insulating oils is reported with high insulating performance [1, 2]. Therefore, combination of Nomex® and flame-resistant insulating oils is a promising transformer which has high fire prevention and high insulating performance.

7. CHEMICAL ANALYSES

Chemical analysis of insulating oils can reveal information about their state of degradation [13]. We measured the kinematic viscosity (KV) of fresh and aged oils. Large-capacity power transformers are cooled by circulating insulating oil. If the kinematic viscosity of the insulating oil is high, the cooling performance of the transformer may be reduced. The total acid number (TAN) reflects the amount of acidic substances such as degraded acids [13]. Generation of sludge and interfacial tension may be reflected by an increase in TAN.

Tests were carried out in accordance with Japanese Industrial Standard (JIS) K2501 for TAN and JIS K2283 for kinematic viscosity by Japan Analyst Ltd.

7.1 TOTAL ACID NUMBER TEST

Table 3 lists the TAN for fresh oils and oils aged for 1000h. Figure 12 shows the results graphically. Tests were carried out according to JIS K2501 for single measurement. The test method is putting materials in sodium hydroxide until they are neutralized in the test oils (fresh and aging oils). When the test oils were neutralization we used this value as value of TAN.

Table 3. Total acid number.

Temperature [℃]	Total acid number [mgKOH/g]		
	Silicone	Natural ester	Synthetic ester
Fresh oil (0)	0.02	0.24	0.03
130	0.03	1.02	0.09
180	0.07	12.88	3.44

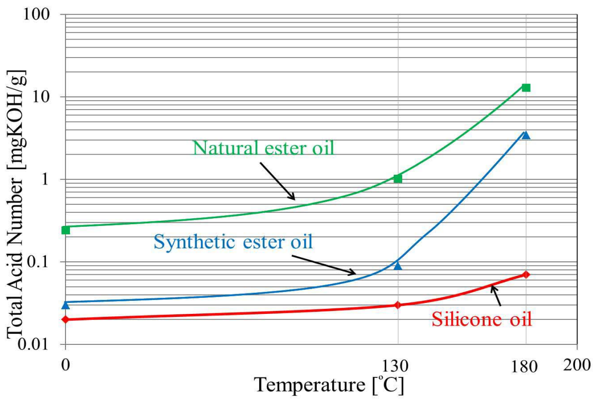

Figure 12. Total acid number characteristics of fresh and aging oils.

The TAN of all oils changed on aging. The increase in TAN on aging was small for silicone compared with the natural and synthetic ester oils, especially when heating temperature was 180 °C. Silicone oils have excellent oxidative stability and therefore long-term heating at a high temperature will only lead to a small degree of degradation. Natural and synthetic ester oils are prone to greater chemical changes compared with silicone oils, especially on heating at 180 °C. And, the oxygen in the oil is cited as a possible cause of the effects. For example, the oxygen contained in the insulating oil and insulators were changed by high temperature and longtime heating for resolution and cohesion. And, there is a possibility that small amounts oxygen get into the tank from the outside during the aging test. It has possibilities that insulating oils become degradation during long time heating. Thus, during long-term heating at high temperature they are likely to degrade. However, this phenomenon is not well understood and will be the focus of future research.

7.2 KINEMATIC VISCOSITY TEST

The kinematic viscosity of insulating oils is an important parameter that indicates potential cooling performance in a power transformer. Kinematic viscosity values for fresh and aged oils are listed in Table 4. Figure 13 shows the kinematic viscosity characteristics according to JIS K2283 for single measurement.

Table 4. Kinematic viscosity of fresh and aging oils.

Temperature [℃]	Kinematic viscosity [mm^2/s (40 ℃)]		
	Silicone	Natural ester	Synthetic ester
Fresh oil (0)	15.04	36.23	28.48
130	15.11	40.13	28.22
180	15.19	809.3	29.40

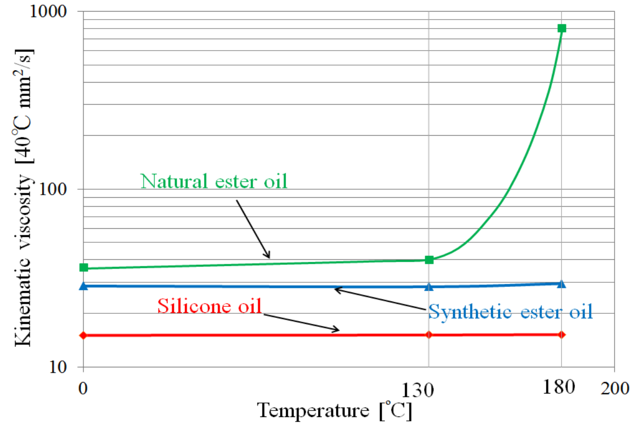

Figure 13. Kinematic viscosity characteristics of fresh and aging oils.

Kinematic viscosity values show in ascending order to silicone oil < synthetic ester oil < natural ester oil. Silicone and synthetic ester oils are constant kinematic viscosity value in the fresh and aging oils. Kinematic viscosity value of silicone oils are small compared with ester oils.
Moreover, the kinematic viscosity of natural ester oils is increasing when it is heated at high temperature for a long time. Especially, it shows a rapid kinematic viscosity value change in heating temperature at 180 °C. Natural ester oils are made from soybean. Thus, in case of long-time heating at high temperature, they are thought to be retrograded to the long-time heating at high temperature. And kinematic viscosity of natural ester oil is increased by the presence of oxygen [14].

We think about the relationship between breakdown voltage and total acid number. As been described in Chapter 6, the breakdown voltage and total acid number are related. All aging oils tick up total acid number compared with fresh oils. The breakdown voltage is reduced by a rise in total acid number of insulating oils. Therefore, silicone and ester oils are thought to decrease by dielectric breakdown voltage. Comparing the characteristics of dielectric breakdown voltage and total acid number, ester oils have been changed both characteristics when heated at 180 ℃. In comparison with fresh and aging oils, total acid number of ester oils is changed. Moreover, breakdown voltage is reduced when the total acid number increases.

8 BURNING CHARACTERISTICS

If there is strong wind, mineral and ester oils will burn with a strong flame until the oil burns out, but silicone oil will extinguish after several minutes. Because when silicone oil is ignited, a white oxide film (SiO_2) will immediately form on the surface, it inhibits oxygen supply so that the flames gradually disappear. Mineral oil and ester oils have same burning behavior however the flash point is different. If the fire accident occurs, it may be unable to suppress the fire. In case of applying silicone oil to the transformer, it may be able to the scale suppression of fire compared with mineral and ester oils. Therefore, silicone oil has superior flame resistance properties compared to mineral and ester oils.

9 CONCLUSION

The authors investigated the thermal degradation characteristics of insulating oils. The color change of silicone oil was smaller than that of natural and synthetic ester oils both before and after aging. Moreover, the decrease in BDV was smaller for silicone oil than for natural and synthetic ester oils both before and after aging. The BDV value of silicone oil is also small. Also, these oils have variation in value of BDV. When silicone oil compares with any other oil , the variation in value of BDV is smaller. The tensile strength of aramid paper did not decrease during testing. Therefore, silicone and ester oils in combination with aramid paper can be operated at higher temperatures than that of mineral oil [2, 15]. Thus, it is possible to reduce the amount of oil inside a transformer, which contributes to miniaturization of equipment and cost reduction. The tests time we performed was shorter than the running time of transformer. Therefore, tests of longer duration are required to gain an insight into the detailed degradation characteristics. However, the insulating performance and color of ester oils change after a short aging time. Therefore, it is likely that this tendency will become prominent in longer tests. The suitability of ester oils for long-term operation at high temperature remains to be clarified in future research.

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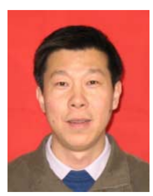

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