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Measurement of Electrical Insulating Oil Oxidation by Evaluating the UV Fluorescence Emission Ratio

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Abstract – In this work, a new fluorescence emission measurement technology was introduced and experimentally compared with other measurement methods, such as the titration method and IR spectroscopy, to validate it for the oil oxidation measurement of electrical insulating oil. The oxidation characteristics of insulating oil were found to be fairly represented by the titration method and IR spectroscopy, and the results are comparable to a change in the fluorescence emission ratio that is defined as the shift in fluorescence intensity in the measured wavelength range. The result also shows that by the measurement of fluorescence emission ratio, it is possible to detect the oxidation of oil relatively earlier than by other methods. This study suggests that the developed technology can provide sufficient information for evaluating the insulating oil quality, and that the developed FER sensor can be used as an effective condition monitoring device of electrical insulating oil oxidation.

Keywords – electrical insulating oil, oxidation, UV fluorescence, sensor, monitoring

1. Introduction

It is important to perform an analysis of insulating oils, for the purpose of garnering information about the oils themselves as well to enable the detection of possible problems such as contact arcing, aging insulating paper and other latent faults. Analysis is an indispensable part of a cost-efficient electrical maintenance program[1].

By accurately monitoring the condition of the oil, sudden faults can be discovered in a timely fashion and outages can potentially be avoided. Furthermore, an efficient approach to maintenance can be adopted and optimum intervals determined for necessary replacements.

Similar to industrial oils, transformer oils are oxidized under the influence of excessive temperature and oxygen, particularly in the presence of small metal particles that act as catalysts and which, result in an increase in the (total) acid number, owing to the formation of carboxylic acids[2]. Further reactions can result in sludge and varnish deposits, and additionally, in increased acidity formation, which has a damaging effect on cellulose paper.

It is known that oil degradation also produces charged by-products, such as acids and hydro peroxides, which tend to reduce the insulating properties of the oil. An increase in the acid number is often accompanied by a decrease in dielectric strength and increased water content[3]. For these reasons, oxidation of electrical insulating oil needs to be monitored while it is in operation.

Methods of analyzing physical and chemical parameters of insulating oil, such as basic appearance (color), water content, and the acid number, have been used to determine oil degradation. These methods have formed a core part of the preventive maintenance of electrical insulating oil thus far[4]. Nonetheless, these methods are limited to off-line analyses for laboratory use,

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whereby it is not possible to provide an early warning before any failure due to the oxidation of electrical insulating oil occurs. Therefore, on-line monitoring technology for evaluating insulating oil degradation is crucial.

In this work, an apparatus is developed to measure the oxidation of electrical insulating oil. The apparatus can be mounted onto mechanical devices for detecting the intensity of fluorescence light reflected from the oil in real time, and this detected intensity is an indication of the extent of oil oxidation. The developed apparatus evaluates the degree of oil oxidation of test oils, based on the UV fluorescence emission ratio. The test results obtained herein are compared with those obtained from other measurement methods such as the titration method and IR spectroscopy.

2. Fluorescence Emission Ratio Technique and Detector for Oil Oxidation Monitoring

All molecules absorb light but only a limited number of molecules emit light as a result of absorption of light from other sources[3]. Aromatic hydrocarbons, polyphenyl hydrocarbons, and compounds with a carboxylic group are organic fluorophores. The phenomenon of fluorescence in organic matter occurs due to the emission of photons by fluorophores when excited by electromagnetic radiation. Fluorophores are able to absorb incident energy, which allows electron transfer from a fundamental energy state to an excited state. The return to the ground state may then produce a luminescence phenomenon such as fluorescence when the time scale is sub-nanosecond. This de-excitation mechanism is not the only one possible, and its efficiency depends on the chemical nature of the compounds and their structural environment. Fluorescence of molecules is related to the energy transition phenomenon in the π-orbitals of the C=C bonds. Moreover, the conjugated π-systems require a lower energy than isolated bonds because of higher π-electron mobility and are therefore readily activated. These considerations designate the aromatic and polyaromatic compounds as the main source of fluorescence properties of the sedimentary organic matter[5]. Oxidation of aromatic molecules leads to an overall increase in polarity, and it results in a relative increase in the absorption and emission at high wavelengths and, therefore, causes a spectral shift of emission intensity.

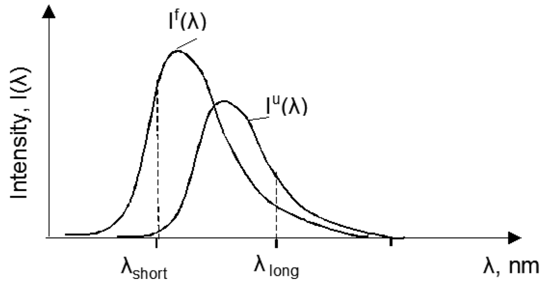


Fig. 1. Fluorescence spectra of fresh $I^f(\lambda)$ and used $I^u(\lambda)$ oil[3].

We propose that this shift of the intensity of fluorescence emission phenomenon be used to evaluate oil degradation. The ratio of intensity at long to short wavelengths referred to as the fluorescence emission ratio (FER). Using fresh oil as a reference baseline, the shift phenomenon characterizing oil degradation is observed as a change in the FER parameter. The FER technique is based on measuring fluorescence intensities in three wavelength ranges, and it consists of the following steps. For fresh oil, the fluorescence emission in red, green, and blue (RGB) wavelengths are measured using color sensor output currents (I) in red I_R, green I_G, and blue I_B wave ranges. The two largest values of $I_{\lambda long}$ and $I_{\lambda short}$ are determined, where $I_{\lambda long}$ is the long wavelength color output current similar to I_R or I_G and $I_{\lambda short}$ is the short wavelength color output current similar to I_G or I_B as shown in Fig. 1. The FER parameter is calculated from the color sensor output current (I) as follows[3,6,7]:

$$FER = \frac{I_{\lambda long}}{I_{\lambda short}} \qquad (1)$$

The higher FER value should correspond to a higher level of oxidation. The obtained FER (Eq. (1)) is compared with a predetermined threshold, and if the

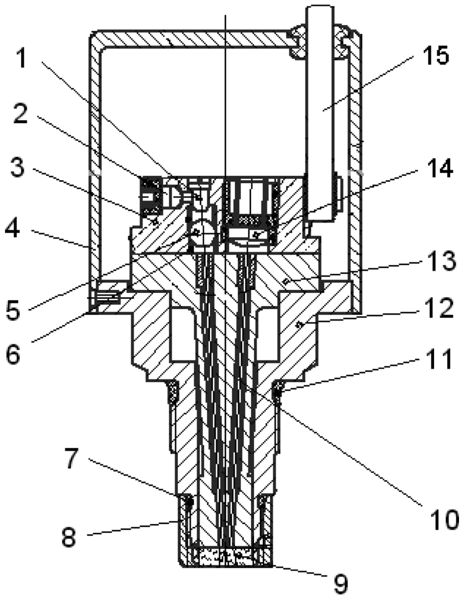


Fig. 2. FER detector design with optical fibers: 1 – UV diode, 2 – feedback photodiode, 3 – bush, 4 – cover, 5 – ball lens, 6 – insert, 7 – O-ring, 8 – nut, 9 – optical window, 10 – optical fibers, 11 – O-ring, 12 – housing, 13 – fiber holder, 14 – RGB sensor, 15 – electric cable[2,3].

obtained FER is below the threshold, then the oil is in good condition; otherwise, the oil condition is unacceptable. This method was used to evaluate the degree of oil oxidation level, and in this measurement, absorption of optical radiation by the oil does not need to be accounted for.

A low cost device based on this shifted phenomenon, as shown in Fig. 2, was developed in this work with a three-color sensor as photo-receiver that detects optical light intensity in three wavelengths ranges—red, green, and blue.

The radiation from the UV diode (1) passes through the bifurcated optical fiber and optical window (9) to the test oil. A ball lens (5) is used to focus the UV diode radiation at the optical fiber end. The optical fibers are mounted in the fiber holder (13), which are inserted into housing (12). An optical window is fixed to the housing (12) by a nut (8). The optical fiber transmits the fluorescent emission from the test oil to the RGB sensor (14). A photodiode (2) is applied to stabilize the UV radiation feedback. The UV diode, RGB sensor, and feedback diode are cable-connected to an electronic block (not shown in Fig. 2). O-rings (7) and (11) prevent oil leakage into the sensor. A cover (4) is used to protect the detector. The electronic microcontroller, amplifier and power PCBs, and an LCD panel are housed in a box, cable-connected to the detector probe (15). The fluorescence emission from the test oil is measured on a RGB sensor (14), and then the FER is calculated by an embedded microprocessor in the device[7]. In this work, $I_{\lambda long}$ was selected as I_G and $I_{\lambda short}$ was selected as I_B, for the evaluation of the FER. Information of the fluorescence analysis technology used in this work and the sensing device used to implement the idea can be accessed in other works [6,7].

3. Oxidation Test Results

The test oil used in this experiment is Mictrans KS 2301, 1-2 electrical insulating oil (Michang oil, kinematic viscosity: 9.00 cSt @ 40°C, initial TAN value: 0.0055 mgKOH/g, water content: less than 15 ppm, life criteria: TAN less than 0.24).

For preparing an artificially oxidized oil sample, test oil was oxidized by ASTM 2440-99[8], with some modifications, as follows: 500 ml of test oil was heated to 110±0.5°C, and mixed with 1.5 L/h of 99.4% pure oxygen in the customized oil apparatus, as shown in Fig. 3. After the oxygen rushed into the drying tower, it entered the micro-bubbler and immediately contacted the copper coil (180 cm long). The oil was stirred at 300 rpm for uniform oxidation of the oil.

Every 12 hours, a small portion of test oil sample was momentarily extracted from the apparatus in order to measure the level of oxidation of the oil. The oxidation levels of test oil samples were also measured using two types of commercially available lubricant monitoring sensors (TAN test cell of Kittiwake Co. and Fluidscan of Spectro Co.) in addition to, the FER sensor developed in the present work, and they were analyzed by the FTIR of Perkin Elmer Co. The TAN test cell (FG-K25196-KW) uses a titration method

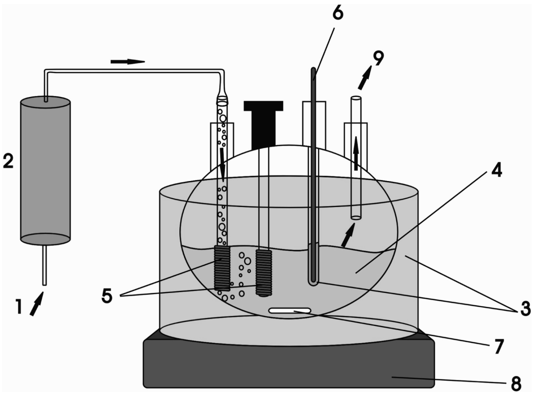


Fig. 3. Test oil oxidation apparatus: 1 – oxygen in, 2 – drying tower, 3 – aging bath, 4 – test oil, 5 – copper catalyst, 6 – thermocouple, 7 – magnetic stirrer, 8 – heater and stirrer, 9 – oxygen out.

Table 1. Measurement results

Oxidation Time, hr	FER	Fluidscan®(Q1000)		TAN by Titration
		Oxidation	TAN*	
0	0.00	0.0	0.00	0.000
108	0.03	0.0	0.00	0.042
204	0.06	0.0	0.00	0.042
408	0.06	0.0	0.00	0.048
600	0.45	0.8	0.02	0.177
822	0.64	10.2	1.23	1.53

*TAN of Fluidscan is measured in a substraction mode, i.e., that the measured value denotes the increase in the TAN of the test oil as compared to that of fresh oil.

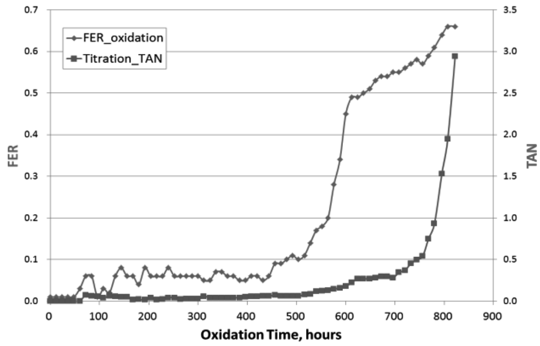
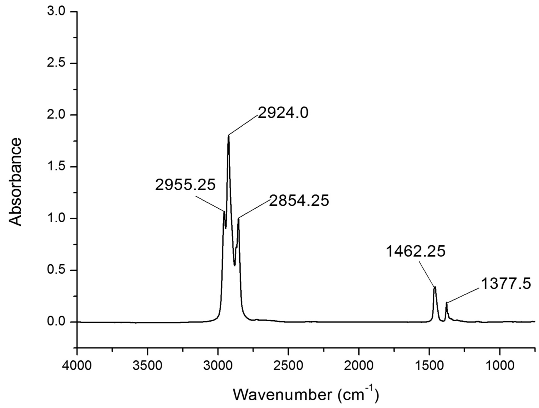


Fig. 4. FER versus TAN by titration method.



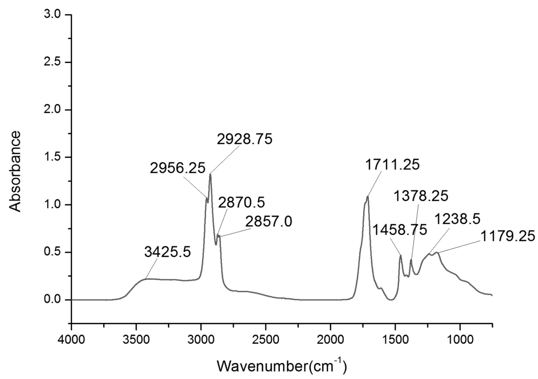


Fig. 5. FTIR spectra of fresh insulating oil (top) and FTIR spectra of oxidized insulating oil (bottom).

based on ASTM D974-11[7,9]. It operates by measuring the color change caused by acid in the test oil sample. In this work, a 20 μL pipette was specifically used for the TAN test in order to increase the titration accuracy. Fluidscan®Q1000 is a handheld mid-infrared spectrometer based on ASTM standard practices (E2412-04), that measures the total acid number (TAN), oxidation level, and other related parameters [9-12]. After the measurement, the oil sample was returned to the oil apparatus.

Test results are summarized in Table 1, the data from which shows that the test oil started to degrade primarily because of the simultaneous anti-oxidant depletion. The degraded oil gradually caused an increase in the acid number, and it was found that oil degradation initiated approximately at the 600-hour mark of oil oxidation.

Once oil oxidation was initiated, the acid number increased abruptly, as shown in Fig. 4. It was found that the measured FER parameters generally showed highly similar results with those obtained from Fluidscan®Q1000 and titration methods. The FER parameter seems to increase relatively earlier than TAN, providing an early warning of oil oxidation. It is believed that the FER parameter shift with the oil oxidation precedes the increase in the acid number of the oil sample. It is worth while noting that the fluorescence of oxidized oils relates to energy transition phenomena in the π orbitals of C=C bonds of organic matters, while the acid number of oil relates to the formation of acidic matters to be titrated by the added KOH solution. This result suggests that the proposed FER sensor could be an effective indicator of the oil oxidation level. FTIR analysis of oil sludge samples formed at 822 hours clearly showed a significant increase in the carbonyl peaks (-C=O, near 1700~1750 cm^{-1}) and hydroxide peaks (-OH, near 3300~3500 cm^{-1}), which are indications that the oil was oxidized, as shown in Fig. 5.

4. Conclusion

Initiation of oil oxidation in electrical insulating oils is most important to monitor in power transformer equipment, because it indicates that the oil can be expected to abruptly degrade thereafter. In this work, results obtained using a newly developed FER sensor result were compared with the results obtained by other measurement methods to determine whether the FER could be used to provide an effective method to monitor oxidation of electrical insulating oils. It was found that the measured FER parameter could be used to analyze the oil oxidation in a simple and effective manner.

Results also showed that the newly developed apparatus used for measuring the FER parameters had better sensitivity in quantitatively evaluating the electrical insulating oil oxidation. Therefore, it is expected that the developed device could be used as a cost-effective and reliable, continuous monitoring tool for electrical insulating oils in an on-line application.

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