J Electr Eng Technol Vol. 8, No. 3: 588-594, 2013
http://dx.doi.org/10.5370/JEET.2013.8.3.588

ISSN(Print) 1975-0102
ISSN(Online) 2093-7423

Study on Aging Characteristics and Chemical Composition of Hydrogenated Transformer Oil

Yi-Hua Qian†, Yi-Bin Huang*, Qiang Fu and Zhen-Sheng Zhong***

Abstract – Under the condition of Baader aging, the chemical composition variation and the influence of transformer oil aging on electrical properties such as dielectric loss factor and physic-chemical properties such as interfacial tension were studied in the aging precess. Moreover, the correlation between hydrogenated transformer oil electrical and physic-chemical properties and its chemical composition variation were also investigated. The results show that these parameters of physic-chemical and electrical properties of hydrogenated transformer oil relate to each other and have closed correlation with chemical composition.

Keywords: Baader aging, Hydrogenated transformer oil, Chemical composition, Electrical and physic-chemical properties

1. Introduction

As one of the most important insulating medium, transformer oil undertakes as insulation, cooling, extinguishing arc and information carrier in high voltage electrical equipment, especially in the power transformer. So transformer oil should have excellent electrical and physicochemical properties. With the rapid development of social economy and the construction of national key projects such as the west-to-east electricity transmission project, there is an increasing demand of transformer oil. And in order to ensure the economic and safe operation of high-voltage and large-capacity transformers, more serious requirements are presented on the quality of transformer oil [1-2]. Therefore, transformer oil is expected to not only play the fundamental role of insulation and cooling, but also need to have excellent antioxidant and anti-aging properties [3].

Hydrogenated transformer oil is a type of oil refined by chemical modification under severe condition. The comparative study on electrical and physicochemical properties of domestic hydrogenated transformer oil with four other kinds of domestic and foreign naphthenic oil has been performed in this group[4]. It has been proved that the former has excellent electrical and physicochemical properties which could meet the demands of power transformer oil. The anti-oxidation and anti-aging properties of hydrogenated transformer oil and the relationship between the performance and its chemical composition were further studied, which played an important role in the application of hydrogenated transformer oil.

At present, the aging resistance performance of transformer oil is researched mainly through the accelerated aging method. Lian group put the transformer oil in aging oven at high temperature of 115 °C and studied the aging status by determining oil samples' properties at regular intervals [5]. In order to accelerate deterioration, Wang et al. immersed copper wire which were prepared beforehand in transformer oil and aged them at high temperature(115 °C) in a constant temperature apparatus [6]. Shao group studied the anti-oxidation and anti-aging properties of transformer oil via rotary bomb oxidation test, however she did not research the variation during aging [7].

In this paper German Standard DIN 51554-1978 was referred to, the chemical composition variation and the influence of transformer oil aging on electrical and physic-chemical properties were studied in the aging process [8]. In addition, the correlation between hydrogenated transformer oil's properties and its chemical composition variation were also investigated.

2. Experiment

2.1 Materials

Hydrogenated 25th transformer oil purchased from market.

2.2 Instrumentation and analysis

2.2.1 Aging Instrument

Apparatus for the determination of aging characteristics of lubricating oils. The instrument was manufactured

† Corresponding Author: Electric Power Research Institute of Guangdong Power Grid Corporation, China. (qianyh2001@163.com)
* College of Chemistry and Chemical Engineering, South China University of Technology, China. (ybhuang615@126.com, chszhong@scut.edu.cn)
** Electric Power Research Institute of Guangdong Power Grid Corporation, China. (fuqiang7293@163.com)
Received: August 1, 2012; Accepted: October 19, 2012

strictly according to the test methods specified in DIN 51554 and it was made in Italy.

2.2.2 Aging Test

German Standard DIN 51 554-1978 was referred to [8]. As shown in Fig. 1, 60 mL of transformer oil was taken accurately into the test tube, whose upper part connected with Liebig condenser to avoid the light component of oil losing when heating. Six test tubes were accommodated in the instrument at the same time. Copper coils were cleaned with sandpaper, filter paper and washed with toluene orderly, and then dried at 105 °C for 10 minutes. As shown in Fig. 2, the copper coils connected to the up-and-down devices and went up and down, outside and inside the oil sample, whose motion frequency was 25 rpm. The aging tests were carried out at constant aging temperature of 110 °C for 28h, 56h, 84h, 112h, 140h respectively. After aging the oil samples were measured as follows.

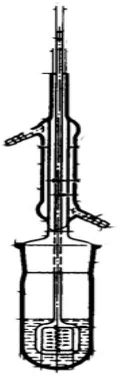

Fig.1. Baader Aging Tube

Fig. 2. Baader Aging Device

2.2.3 Determination of oil samples after aging

- Determination of group component: The tests were carried out according to DL/T 929-2005 [9].
- Determination of dielectric loss factor: The tests were carried out according to GB 5654-2007 [10].
- Determination of volume resistivity: The tests were carried out according to DL 421-91 [11].
- Determination of relative permittivity: The tests were carried out according to DL 429.9-91 [12].
- Determination of interfacial tension: The tests were carried out according to GB/T 6541-86 [13].
- Determination of total acid value: The tests were carried out according to GB/T264-83 [14].
- Determination of kinematic viscosity: The tests were carried out according to GB 265-88 [15].

3. Results and Discussion

3.1 Variation of chemical component with time

Generally, transformer oil contains cycloalkane (C_N), alkane (C_P) and aromatic hydrocarbon(C_A). Variation must have occurred in carbon group component in aging process that would influence on the performance of transformer oil inevitably. Based on the aging method mentioned in 2.2.2, aging test was conducted and variation on carbon group component was also studied. The results are shown in Table 1.

Table 1. Variation on Carbon Group Component with Time

Component	0h	28h	56h	84h	112h	140h
C_A%	0.23	0.23	0.23	0.23	0.23	0.23
C_P%	56.71	57.82	58.34	59.11	59.24	60.21
C_N%	43.06	41.95	41.43	40.66	40.53	39.56

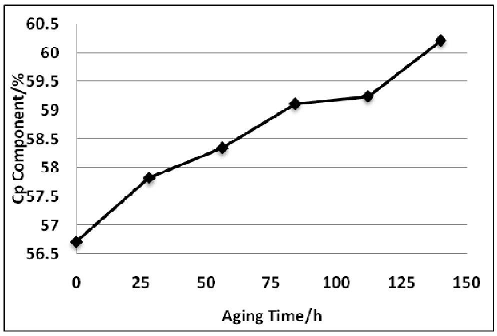

Fig. 3. Variation on alkane

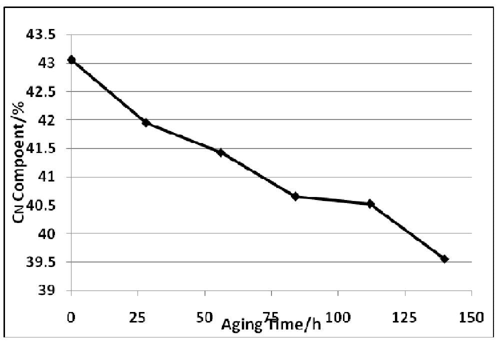

Fig. 4. Variation on cycloalkane

As shown in Table 1, carbon group component of hydrogenated transformer oil shows obvious and regular changes. C_A stays constant while C_P increases gradually and C_N decreases gradually along with the aging time. After 140 hours of aging, C_P increases 6.2% and C_N decreases 8.1%. As illustrated in Fig. 3 and Fig. 4, the amplitudes of variation of C_P and C_N show accelerated increasing tendency after 112 hours of aging. It seems that 112 h is a notable aging inflection point.

According to DL/T 929-2005, the carbon group composition value is calculated by the formulas

$$C_A\% = \mathbf{10.32} \times \frac{A_{1610}}{l} + \mathbf{0.23} \quad (1)$$

$$C_p\% = \mathbf{6.9} \times \frac{A_{720}}{l} + \mathbf{28.38} \quad (2)$$

$$C_N\% = \mathbf{100} - (C_A\% + C_P\%) \quad (3)$$

In the formulas, A_{1610} is the absorbance at 1610 cm^{-1}, A_{720} is the absorbance at 720 cm^{-1},l is the length of liquid pool.

Theoretically, the aromatic hydrocarbons are more active than the cycloalkanes and easier to oxidize to further generate the resin and sludge [16]. And the content of C_A must have changed with aging time. In this experiment, the value of C_A does not change before and after 140 hours of aging. According to the formula (1), the content of C_A in the aging process remained 0.23, because there was no absorbance at 1610cm^{-1}. It is probably because the aromatic content of hydrogenated transformer oil is extremely low due to its special production techniques and lower than the detection limits of infrared spectrum method. So it cannot be detected by FT-IR even though the aromatic hydrocarbons have a little change. Therefore, the determination value of A_{1610} always maintains constant of zero and the value of C_A does not change.

C_p increases gradually while C_N decreases with the aging time. It can be seen that the sum of the three kinds of carbon group composition is 100% from the formulas (1)(2)(3). The alkane component is on the increase under the Baader condition and C_A maintains constant. Therefore, the cycloalkane component reduces gradually.

Fig. 5 shows the infrared spectroscopy of hydrogenated transformer oil before and after aging. The six spectral curves from bottom to up(at 3650 cm^{-1}) corresponded to the new oil, the oil after aging 28h, 56h, 84h, 112h, 140h respectively. The aging of transformer oil could be analyzed by infrared spectroscopy, according to absorption peak of antioxidant T501 at 3650 cm^{-1} and the characteristic absorption peak of aging products such as acids, ketones, esters and so on at 1600-1800cm^{-1} [17-18]. As shown in Fig. 5, the six curves are almost overlapped and there are no new functional groups to produce, indicating that there are almost no aging products such as acids and ketones and the consumption of antioxidant is little.

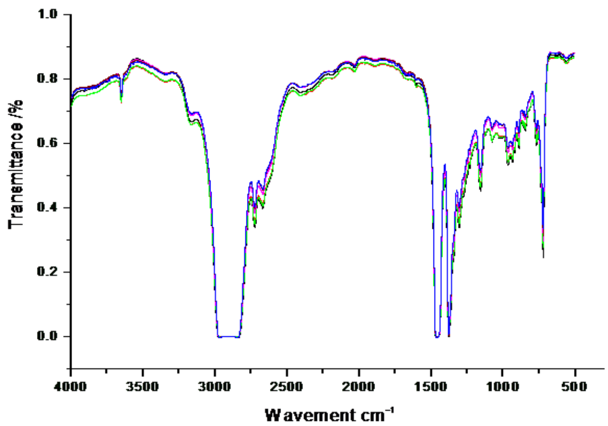

Fig. 5. IR Spectrum of Hydrogenated Transformer Oil Before and After Aging

3.2 Color variation with aging time

The color variation of transformer oil can reflect the aging degree of oil in the power transformer. New transformer oil is usually faint yellow. The progressive change of the color indicates that the transformer oil has been deteriorated. This color change is essentially due to the oxidization of the oil in service which, consequently, leads to the formation of the acidic products.

The influence of aging on color of hydrogenated transformer oil is shown in Fig. 6. As shown in Fig. 6, the color of hydrogenated transformer oil has no change along with the aging time. Due to its higher refining degree, as illustrated in Table 1, hydrogenated transformer oil has low content of polycyclic aromatic hydrocarbons which has poor color stability, so the color almost has no change in the Baader aging process.

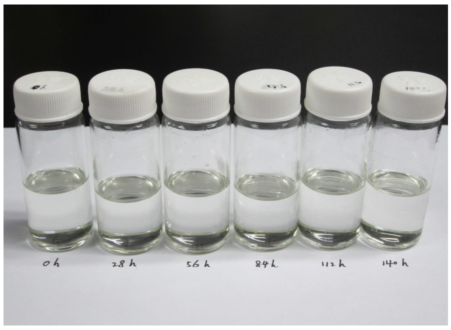

Fig. 6. The Influence of Aging on Color

3.3 Dielectric loss factor variation with aging time

As shown in Table 2, at the beginning of oil aging, tanδ increases slowly, and the amplitude of variation is weak. It increases 61.5% from 0h to 84h at an average rate of 0.7% per hour. The change becomes greater after ageing 84h, which is the beginning of a vicious circle. Tanδ increases 56.4% from 84h to 112h at an average rate of 2.0% per hour. And it even increases 100% from 112h to 140h at an average rate of 3.6% per hour.

It is generally acknowledged that dipole loss increases because of the medium heterogeneity. After aging, as insulating medium, the composition of the oil would change. Under the influence of alternating electric field periodic polarization, it would absorb energy of the electric field and convert into heat, leading to the intensity of joule thermal reaction, resulted in the dielectric loss in radiation degree, thermal reaction and some kinds of thermal change. Thus the oil was deteriorated accelerated and tanδ increases rapidly[17].

As shown in Table 1 and Table 2, the curves of tanδ and C_N both have inflection point after aging 84−112 hours. It could be inferred that the reduction of cycloalkane composition of hydrogenated transformer oil would lead to the deterioration of oil electrical properties during aging.

Table 2. Dielectric Loss Factor Variation with Time

Aging Time	Dielectric Loss Factor (tanδ)	Amplitude of Variation
0h	0.00039	0
28h	0.00045	+15.4%
56h	0.00052	+33.3%
84h	0.00063	+61.5%
112h	0.00085	+117.9%
140h	0.00124	+217.9%

3.4 Volume resistivity variation with aging time

As a kind of insulating oil, the volume resistivity of transformer oil is the most sensitive to ion conduction loss of oil. Ion conduction is that hydrocarbon molecules and impurities in insulating oil dissociate into ion to form the ion conductance. There are two ways to form ion conductance. Under high temperature, hydrocarbon molecules convert into ion due to the thermal dissociation, resulting in the ionic conductivity. The ionic conductivity is also produced because of the impurities from outside. Generally, a series of oxidation products will form in transformer oil after aging. It will lead to the dramatically increase of ion, which is the main factor to cause ion conduction of insulating oil [19].

The test results are shown in Table 3.

It can be seen in Table 3, at the beginning of oil aging, the volume resistivity varies obviously, decreasing from 609.1 GΩ·m to 450.3 GΩ·m. And the amplitude of variation is -26.1%. And then the variation tends to slow from 56 h to 112 h. The amplitude of variation reduces to -14.9% at the same interval of 56 hours.

Table 3. Volume Resistivity Variation with Time

Aging Time	Volume Resistivity/ GΩ·m	Amplitude of Variation
0h	609.1	0
28h	513.2	-15.7%
56h	450.3	-26.1%
84h	402.2	-34.0%
112h	359.4	-41.0%
140h	320.4	-47.4%

Combined with Table 2 and Table 3, it is shown that the volume resistivity of transformer oil has negative correlation with dielectric loss factor. Combined with Table 1, the correlation between the volume resistivity and C_N cannot be known from the curves at the moment because the inflection points of curves appear at different time.

3.5 Relative permittivity variation with aging time

Relative permittivity is an important parameter to characterize the dielectric or electrical properties of insulating materials, which is commonly expressed by ε. It indicates the dielectric's relative ability of storing electrostatic energy in the electric field. The test results are shown in Table 4.

Table 4. Relative Permittivity with Time

Aging Time/h	0	28	56	84	112	140
Relative Permittivity(ε)	2.07	2.07	2.07	2.07	2.07	2.07

As shown in Table 4, the relative permittivity of transformer oil remains constant during ageing under Baader aging condition. Table 1 shows the obvious changes of carbon group composition before and after ageing, and it seems to indicate the relative permittivity of hydrogenated transformer oil has no correlation with carbon group composition. Or maybe the relative permittivity of hydrogenated transformer oil undergoes a very weak variation, and the composition of carbon group does not vary so greatly as to cause the relative permittivity to change. It is consistent with the view that the relative permittivity is a property of the oil's chemical constitution [20].

3.6 Interfacial tension with time

The interfacial tension of oil is required to rupture the oil surface existing at an oil-water interface. It could reflect the degree of refining and contamination of oil. Interfacial tension is extremely useful for determining the presence of polar contaminants and oil aging products. New oil usually exhibits high value of interfacial tension. Interfacial tension reduces with aging under the influence of combined stresses, oil oxidation, etc. The increase in oxidation contaminants causes more reduction in interfacial tension. This may be due to high affinity towards water and oil molecules[21].

Table 5 exhibits the variation of interfacial tension with time in accelerated degradation test. As shown in Table 5, interfacial tension declines gradually with the aging time. The interfacial tension shows a large change for 112 hours of aging. Combined with Table 1 and Table 2, we could know the curves of interfacial tension, tanδ and C_N all have inflection point after aging 84-112 hours.

Table 5. Interfacial Tension Variation with Time

Aging Time	Inerfacial tension/ $mN{\cdot}m^{-1}$	Amplitude of Variation
0h	52.1	0
28h	50.1	-3.8%
56h	49.3	-5.4%
84h	48.8	-6.3%
112h	47.5	-8.8%
140h	45.8	-12.1%

3.7 Variation of total acid value with time

Total acidy value is an important index which can demonstrate the acid number in the oil. The acid, whether existing in the new oil or produced in the aging oil, could improve the conductivity of oil and facilitate the solid fiber aging, leading to the damage of equipment. Meanwhile it would react with metal material to produce metal salts which could accelerate oil aging as catalyst. Therefore, controlling the total acid number in the oil is a critical measure to extend the service life of transformer oil and electrical equipments.

As shown in Fig. 7, the total acidy value has no changes initially but begins to increase after 56 hours of aging. It indicates that transformer oil deteriorated slowly at the beginning of aging and few acidic products form. But the acidic products would have a dramatic rise after aging for a length of time.

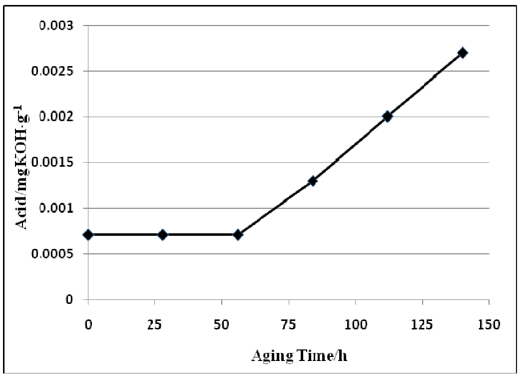

Fig. 7. Variation of total acid value with time

3.8 Variation of kinematic viscosity with time

The viscosity of dielectric coolants within the range of normal operating temperatures is important because it can impact both the cooling and performance of some internal components. The oil closed to the windings in the field transformer flows up at higher temperature while the oil at lower temperature flows to bottom from the wall. The heat scattered from windings in this way. So transformer oil with lower viscosity has better cooling effect. The increase of viscosity, which has negative effect on load and efficiency, is adverse to the safe operation of the unit. Therefore, it is essential for us to control the viscosity of transformer oil in service.

Table 6. Kinematic Viscosity Variation with Time

Aging Time	kinematic viscosity /$mm^2{\cdot}s^{-1}$	Amplitude of Variation
0h	9.408	0
28h	9.426	+0.19%
56h	9.492	+0.89%
84h	9.561	+1.63%
112h	9.591	+1.95%
140h	9.838	+4.57%

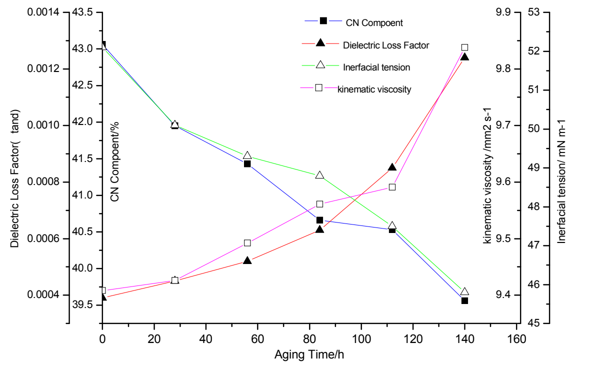

Fig. 8. Influence of Aging on C_N, tanδ, interfacial tension and kinematic viscosity

Table 6 exhibits the variation of kinematic viscosity with time in the test. As shown in Table 6, kinematic viscosity increases gradually with aging time. It increases slightly at an speed of 0.017% per hour initially but rises sharply at an speed of 0.094% per hour after 112 h of aging, marking an approximate 5.5-fold increase.

As described in Fig. 8, the results show that under Baader aging condition, the inflection points appeared in the aging curves of cycloalkane composition, interfacial tension, kinematic viscosity and dielectric loss factor almost at the same time. And these parameters of physic-chemical and electrical properties of hydrogenated transformer oil relate to each other and have closed correlation with chemical composition.

4. Conclusion

Under Baader aging condition, the aromatic composition almost stays constant and the alkane composition increases gradually while the cycloalkane composition decreases gradually along with the aging time. The color of hydrogenated transformer oil has no change with aging. Total acid value and kinematic viscosity increase gradually while interfacial tension decreases gradually during aging. The dielectric loss factor rises slowly at the beginning of aging, and start to increases greatly after 112 hours of aging. The volume resistivity declines greatly at the beginning of aging, and start to reduces slowly after 56 hours of aging. The volume resistivity of hydrogenated transformer oil has negative correlation with dielectric loss factor.

The curves of tanδ, C_N, interfacial tension and kinematic viscosity all have inflection point after aging 84−112 hours. These parameters of physic-chemical and electrical properties of hydrogenated transformer oil relate to each other and have closed correlation with chemical composition.

Acknowledgements

This work is financially supported by Key Research Project of Guangdong Power Grid Corporation (K-GD2011-377).

References

[1] Ruijin Liao, Fumin Sang, Gang Liu, Lijun Yang. "Study on Neutral Acid and Water Dissolved in Oil for Different Types of Oil-paper Insulation Compositions of Transformers in Accelerated Ageing Tests," *Proceeding of the CSEE*, Vol. 30, No. 4, pp. 125-131, 2010.

[2] Chao Tang, Ruijin Liao, Feilong Huang, Lijun Yang, Mengzhao Zhu. "The Breakdown Voltage of Power Transformer Insulation Paper After Thermal Aging," *Transactions of China Eletrotechnical Slciety*, Vol. 25, No. 11, pp. 1-8, 2010.

[3] Liao Ruijin, Jian Hao, Shuaiwei Liang, Mengzhao Zhu, Lijun Yang. "Choice of Antioxidants Added in Insulation Oil and Its Anti-oxidant Synergistic Effect," *High Voltage Engineering*, 124-131, Vol. 38, No. 1, pp. 124-131, 2012.

[4] Yihua Qian, Haiyan Wu, Wei Su, Yibin Huang, Zhensheng Zhong. "Comparative Study on the Electrical Properties of Several Kinds of Domestic or Imported Transformer Oil," *Power System Technology*, Vol. 35, No. 2, pp. 770-773, 2011.

[5] Hongsong Lian, Dongsheng Zheng. "Ageing Tests of Domestic Made EHV Transformer Oil of Hydrogenated Type and Some Kinds of Imported EHV Transformer Oils," *Electrical Equipment*, Vol. 6, No. 1, pp. 16-18, 2005.

[6] Xianmin Wang, Yongfei Ma, Peng Dou. "Influence of Aging Transformer Oil to Dielectric Loss Factor and Research on Insulation Life Test," *Transformer*, Vol. 8, No. 4, pp. 41-44, 2011.

[7] Lihua Shao. "Research of Large Transformer Oil Anti-oxidation and Anti-aging Properties," *Anhui Chemical Industry*, Vol. 35, No. 6, pp. 43-45, 2009.

[8] DEUTSCHE NORMEN, DIN 51554-1978. "Prüfung der Alterungsbeständigkeit nach Baader Prüfung bei 110°C ".

[9] DL/T 929-2005, "Determination of the Content in Insulating Oil and Lubricating Oil by Infrared Spectrum Method," *National standard of China*.

[10] GB 5654-2007, "Insulating liquids-Measurement of Relative Permittivity, Dielectric Dissipation Factor and d. c. Resistivity," *National standard of China*.

[11] DL 421-91, "Determination of electrical resistivity," *Electric Power Industry Standard of China*.

[12] DL 429.9-91, "Insulating oil dielectric strength test," *Electric Power Industry Standard of China*.

[13] GB 6541-86., "Petroleum products-mineral oils-Determination of interfacial tension of oil against water-Ring method," *National standard of China*.

[14] GB/T 264-83, "Petroleum products-Determination of acid number," *National standard of China*.

[15] GB 265-88, "Petroleum products-Determination of kinematic viscosity and calcuation of dynamic viscosity," *National standard of China*.

[16] Xuyao Qian, "Transformer oil and the related fault diagnosis technology," *Beijing: China Power Press*, pp. 62-63, 2006.

[17] Dou Peng, Daowu Yang, ChengFeng Wang, "The Influence of Transformer Oil Aging to Dielectric Dissipation Factor and Its Insulating Lifetime," *IEEE, Power and Energy Engineering Conference*, pp. 1-4, 2009.

[18] Peng Dou, Daowu Yang, Yi Li, Jie Gong, "Analyze Aging Characteristica of Transformer Oil Based on Infrared Spectroscopy and Chaos Theory," *High Voltage Engineering*, Vol. 35, No. 4, pp. 849-854, 2009.

[19] Hongmei Wang, "Power oil (gas)," *Beijing: Chemical Industry Press*, pp. 92-93, 2009.

[20] Abdi. S, Boubadeur. A, Haddad A. "Influence of thermal ageing on transformer oil properties," *Dielectric Liquids, IEEE International Conference*, pp. 1-4, 2008.

[21] Jashandeep Singh, Yog Raj Sood, Piush Verma, "The Influence of Service Aging on Transformer Insulating Oil Parameters," *IEEE Transactions on Dielectrics and Electrical Insulation,* Vol. 19, No. 2, pp. 421-426, 2012.

Yi-Hua Qian received the B.Sc. degree from Wuhan University. She began her M.S. career from 2000 to 2002 in South China University of Technology. Currently, she is a senior engineer at the Electric Power Research Institute of Guangdong Power Grid Corporation. Her research interests include in technical supervision and management of the power oil and scientific research.

Yi-Bin Huang received the B.Sc. degree from South China Agricultural University. He is currently a post-graduate student in South China University of Technology. His research interests include the power oil and insulating technology.

Zhen-Sheng Zhong received the B.Sc. degree in organic chemistry from Sun Yat-Sen University in China. He is currently a professor in South China University of Technology. His research interests include the power oil and fine organic chemicals.

Qiang Fu obtained his master degree in applied chemistry from the University of Wuhan in China. He is currently a senior engineer of power chemistry at Electric Power Research Institute of Guangdong Power Grid Corporation in China. His research interests include research of insulated oil, solid insulate aging and on-line monitor technical.