

Selection of 2,6-Di-*tert*-butyl-4-methylphenol and High Purity Alkylated Phenyl- α -naphthylamine and Their Synergy Antioxidation Mechanism in Insulation Oil

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In order to improve the oxidation stability of a new insulation oil derived from mineral oil and natural ester, 2,6-di-*tert*-butyl-4-methylphenol (DBPC) and high-purity alkylation- α -naphthylamine (HPAN) have been selected as the composite antioxidant in the oil by using pressure differential scanning calorimetry. Pressure differential scanning calorimetry results show that the composite antioxidant can enhance the oxidation stability of the new insulation oil significantly and make its oxidation stability more superior to mineral oil. Molecular simulation and fourier transform infrared spectroscopy results indicate that it is the synergistic antioxidant effect of DBPC and HPAN improving the oxidation stability of the new insulation oil. At last, a preliminary analysis of the synergistic mechanism of the composite antioxidant was proposed.

Key Words: Oxidative stability, Insulation oil, Composite antioxidant, Molecular simulation, FT-IR, Synergistic mechanism.

INTRODUCTION

Power transformers are one of the most expensive and strategic components of electric power transmission and distribution systems ensuring the safe operation of power grid. Because of temperature, electric field, water, oxygen and other factors influence in the long-running of transformer, the oil-paper insulation which determines the transformer life will be aging gradually. Oil oxidation can generate water, acid and sludge, *etc.* Moisture is recognized to be "enemy number one" for transformer insulation¹. Water is particularly detrimental to both the dielectric properties of oil-paper insulation systems and to its resistance to aging¹. Acids may attack the metallic parts of the transformer and damage the insulation paper. Deposition of the sludge in the iron core or windings of transformer can result in plant failure. All these above may affect the power transformer reliability. Power transformers usually contain several tons of insulating liquid. Thus the fluid filled in the transformer must have good dielectric properties and good oxidation stability as well.

In order to improve power transformer reliability, a special focus has been carried out on insulating materials and especially on insulating oils. Many works have been done to improve the properties of mineral oil by mixing it with other industrial liquids. Natural ester insulating fluid offers fire safety, environment and insulation aging advantages over mineral oil and are

found to be suitable for the use in transformer insulation system^{2,3}. Previous sealed tube aging studies show that the thermal aging rates of virgin paper insulation in natural ester insulating fluid are significantly slower than those in mineral oil⁴⁻⁶. Taking into account the properties of mineral oil and natural ester, we developed a new type of insulation oil with good performances derived from mineral oil and natural ester⁷.

This study aims at the optimization of power transformer insulation *via* improving the new insulation oil oxidation stability. As natural esters are more biodegradable than mineral oil, they tend to have lower oxidation stability. Their oxidation stability is often enhanced by the use of antioxidants. The objectives of this paper are: (1) to improve the new insulation oil oxidation stability by selecting the best composite antioxidant added into the new insulation oil; (2) to confirm the synergistic effects of composite antioxidant by molecular simulation and FT-IR spectroscopy experiments of antioxidants; (3) to analyze the synergistic mechanism of composite antioxidant added into the insulation oil.

EXPERIMENTAL

In this study, the oil samples are new insulation oil (NIO) and new #25 transformer oil (TO). The new insulation oil was developed by our group. It is composed of 80 % mineral oil and 20 % natural ester (extracted olive oil) (v/v). The trans-

former oil was obtained from Chuan-run petroleum chemical limited company (Chongqing, China). The antioxidants of high purity alkylation- α -naphthylamine (HPAN), 2,6-di-*tert*-butylphenol (T511), Rosemary antioxidant (RA), 2,6-di-*tert*-butyl-4-methylphenol (DBPC), alkylation diphenylamine (L57), tea poly-phenol antioxidant (TPA), IGANOX L135 and *tertiary*-butyl-hydroquinone (TBHQ) were obtained from Dongfang Huabo chemical limited company (Chongqing, China).

Experiment equipments are TA instrument DSC2920 (TA, USA), materials Studio 4.0 Software (ACCELRYN, USA), Nicolet 6700 FT-IR spectrometer (Nicolet, USA), Aging oven, Glove operation nitrogen filled case.

Pressure differential scanning calorimetry experiments:

Pressure differential scanning calorimetry (PDSC) was used to select the best composite antioxidant which can be added into the new insulation oil. All PDSC was conducted using the thermoanalysis instrument DSC2920 fitted with a constant-volume pressure cell, using constant heating-rate and isothermal modes. The oxidation onset temperature (OOT) of the oil added antioxidants was got by constant heating-rate PDSC. It was performed on 0.5 mg oil samples in open aluminium pans under 0.5 MPa of high purity oxygen and the oxygen velocity was 150 mL/min. The samples were heated from ambient temperature to 250 °C at a constant heating-rate of 10 °C/min. The onset points of oxidation were calculated by extrapolation from the maximum heat peak to the extrapolation of the baseline. The oxidation inducement time (OIT) was got by isothermal PDSC. Isothermal PDSC of some representative samples were performed on 0.5 mg samples in open aluminium pans under 0.5 MPa of high-purity oxygen and the oxygen velocity was 150 mL/min. Representative samples were heated from room temperature to the stated isothermal temperature 185 °C at a heating-rate of 50 °C/min. And then they were heated continuously until an exothermic peak of oxidation was measured.

Molecular simulation experiments: Molecular simulation (MS) techniques uses atomic models to simulate the structural behaviour of molecule and then simulate physical and chemical properties of materials. Molecular simulation can explain the relationship of material microstructure and macroscopic properties and can simulate the physical phenomena or physical processes which the experimental methods are unable to examine. In this paper, molecular dynamics method was explored. All the geometry optimization and energy minimization calculations were carried out under COMPASS force field by the Accelrys materials studio 4.0.

The best composite antioxidant selected by PDSC is composed of antioxidant A and B. First, model A or B was constructed by MS software and then 5000 step energy minimum was conducted in order to analyze the structure of antioxidant A or B and study if there is hydrogen exiting in antioxidant A or B. Second, model mixture of A and B was constructed. Energy minimization before the 500 ps molecular dynamics simulation was carried out. The step length was set to 1 fs, every 500 fs trajectory was saved in order to later analysis. When molecular dynamics simulation was carried out, the target temperature was set to 343 K, the NPT ensemble was used in the molecular dynamics simulation.

FT-IR spectroscopy experiments: FT-IR spectroscopy is well known for its molecular related spectrum information. FT-IR spectrum fingerprints can provide information directly related to chemical structure, chemical compositions and impurities in the materials analysis. Technique of attenuated total reflectance was used for studying the antioxidants selected by PDSC during the measurement *via* FT-IR spectroscopy. This method is most suitable for measuring spectrum of liquid sample, which intensely absorb the infrared radiation⁸.

Georgiev and Karamancheva studied the ionol and piperidone by thermal microwave treatment to see if there is chemical reaction occurs between the two compounds and confirm that by FT-IR spectroscopy⁹. In present experiment, we put antioxidant A (3 g) and antioxidant B (3 g) into 250 mL bottle, respectively and heated the bottles at 110 °C. The mixture of A:B in a mass proportion of 1:1 was also added into 250 mL bottle, each bottle contenting 3 g mixture was heated at 90 and 110 °C, respectively. Heating the samples in the aging oven can provide the energy necessary for the performance of the reaction, *i.e.*, the molecules receive additional energy and the reaction speed is manifold increased. The FT-IR spectroscopy experiment of antioxidants heated for different time was to prove that there is no possibility for an interaction to be initiated between antioxidant A and antioxidant B at transformer operating temperature. In this experiment, infrared spectrums were collected on a Nicolet 6700 FT-IR spectrometer and average over 32 scans with a resolution of 4 cm⁻¹. The spectrum observed was 4000-650 cm⁻¹ and each spectrum in this experiment was obtained at room temperature (27 ± 1 °C). OMNIC software was used for display and analysis of collected spectrum. And the molecular modeling results will be also validated by FT-IR spectroscopy experiment.

RESULTS AND DISCUSSION

Best composite antioxidant in the new insulation oil:

The new insulation oil is a mixture of mineral oil and natural ester. It is necessary to consider both oxidation mechanism of mineral oil and natural ester when we select the antioxidants used in the new insulation oil. Recognized mechanism of mineral oil is chain reaction of free radical oxidation: including chain off, chain continuity and chain breaking out. Natural ester consists primarily of triglycerides. Triglycerides are glycerol molecules with three long chain fatty acids attached at the hydroxy groups *via* ester linkages. Unsaturated double bonds in the fatty acids are active sites for many reactions, including oxidation, lowering the oxidation stability of natural ester. The high level of unsaturation, *i.e.*, presence of more double bonds, the more susceptible to oxidation the natural ester becomes. Natural ester oxidation is initiated by formation of free radicals. Free radicals can easily be formed from the removal of a hydrogen atom from the methylene group next to a double bond. Free radicals rapidly react with oxygen to form a peroxy radical. The peroxy radical can then attack another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical, propagating the oxidation process¹⁰.

Antioxidants are usually used to improve the oxidation stability of oils. There are two major classes of antioxidant *viz.*, chain breaking radical scavengers and peroxide decom-

posers¹⁰. Chain breaking antioxidants react with radicals to form stable compounds and prevent propagation of the oxidation reaction. The role of peroxide decomposers is to react with and decompose hydro-peroxides. Hydro-peroxides decomposition by peroxide decomposers, however, results in stable compounds and thus limiting oxidation. Besides, some antioxidants display multifunctional effect. Guzman *et al.*¹¹ have studied the synergistic effects of antioxidants on the oxidative stability of soybean oil and poultry fat-based biodiesel. Peyrat-Maillard *et al.*¹² have studied the synergistic and antagonistic effects of antioxidant activity of phenolic compounds in 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) induced-oxidation. It is known that certain combinations of antioxidants can result in synergism, so the oxidation stability of oil can be improved significantly. In this way, considering DBPC is an antioxidant used widely in mineral oil to resist oxidation, we used PDSC to select the best antioxidant which can be mixed with DBPC. Table-1 shows the PDSC results of different oil samples.

Samples	Samples composition	OOT (°C)
1	New #25 transformer oil (TO)	201
2	TO + 0.8 % DBPC	211
3	New insulation oil (NIO)	195
4	NIO + 0.8 % DBPC	208
5	NIO + 0.3 % DBPC + 0.5 % RA	206
6	NIO + 0.3 % DBPC + 0.5 % L135	206
7	NIO + 0.3 % DBPC + 0.5 % TPA	207
8	NIO + 0.3 % DBPC + 0.5 % TBHQ	207
9	NIO + 0.3 % DBPC + 0.5 % T511	210
10	NIO + 0.3 % DBPC + 0.5 % L57	212
11	NIO + 0.3 % DBPC + 0.5 % HPAN	218

Natural ester is susceptible to oxidation than mineral oil at the same condition. In Table-1, the oxidation onset temperature of new insulation oil is only 195 °C, lower than transformer oil which is 201 °C. Thus a kind of proper antioxidant is required to add into new insulation oil to improve its oxidation stability. Comparing the results of different antioxidants added into new insulation oil, it can be seen that the oxidation onset temperature of sample 11 is 218 and 17 °C higher than oxidation onset temperature of transformer oil and also higher than other samples. The ranking for effectiveness of antioxidants mixed with DBPC is HPAN > L57 > T511 > TBHQ ≈ TPA > L135 ≈ RA. So the raw material of the composite antioxidant should choose DBPC and HPAN.

To evaluate the best concentration of HPAN mixed with DBPC in new insulation oil, we kept the concentration of DBPC 0.3 % in new insulation oil unchanged. We added HPAN into new insulation oil with proportions from 0.1-0.9 %. Table-2 demonstrates that the oxidation stability of new insulation oil is getting better with the increase concentration of HPAN. When HPAN concentration is no more than 0.3 %, the oxidation stability of new insulation oil improved significantly, while HPAN concentration is more than 0.3 %, the oxidation stability improved slowly. The cost of HPAN is much higher than DBPC and HPAN is susceptible to auto-oxidation when its concen-

TABLE-2
OXIDATION ONSET TEMPERATURE
(OOT) OF 12-18 OIL SAMPLES BY PDSC

Samples	Samples composition	OOT (°C)
12	NIO + 0.3 % DBPC + 0.1 % HPAN	205
13	NIO + 0.3 % DBPC + 0.2 % HPAN	212
14	NIO + 0.3 % DBPC + 0.3 % HPAN	217
15	NIO + 0.3 % DBPC + 0.4 % HPAN	218
16	NIO + 0.3 % DBPC + 0.5 % HPAN	218
17	NIO + 0.3 % DBPC + 0.7 % HPAN	219
18	NIO + 0.3 % DBPC + 0.9 % HPAN	219

tration is high. So the best composite antioxidant in new insulation oil is 0.3 % DBPC + 0.3 % HPAN¹³. Table-3 also shows that the oxidation onset temperature and oxidation inducement time of sample 21 are higher than samples 19 and 20. It also indicates that 0.3 % DBPC + 0.3 % HPAN can improve the new insulation oil oxidation stability obviously. The properties of the mixed insulating oil are shown in Table-4.

TABLE-3
OXIDATION ONSET TEMPERATURE (OOT) AND
OXIDATION INDUCEMENT TIME (OIT) OF 19-21
OIL SAMPLES BY PDSC

Samples	Samples composition	OOT (°C)	OIT (min)
19	NIO + 0.3 % DBPC	200	9.2
20	NIO + 0.3 % HPAN	211	20.5
21	NIO + 0.3 % DBPC + 0.3 % HPAN	217	23.8

TABLE-4
TYPICAL PARAMETERS OF CONVENTIONAL MINERAL OIL
AND NEW MIXED INSULATING OIL

Properties	Conventional mineral oil	New mixed insulating oil
Kinematic viscosity 40 °C (mm ² /s)	9.55	12.86
Pour point (°C)	< -29.0	< -25.0
Flash point (°C)	150	147
Acidity (mg KOH/g)	0.00840	0.00730
Breakdown voltage (2.5 mm gap electrodes) (kV)	35.0	58.0
Relative permittivity (50 Hz)	2.13	2.22
Initiative oxidation temperature (°C)	201	217
Biochemical oxygen demand after 5 days (BOD ₅) (mg/L)	185	737

Molecular simulation and FT-IR spectroscopy of composite antioxidant: 0.3 % DBPC + 0.3 % HPAN can improve the new insulation oil oxidation stability obviously. It is presumed that DBPC can react with HPAN and the result could be a new compound with better antioxidation properties. Another presumption is that there is synergism between DBPC and HPAN, which leads to improving the new insulation oil antioxidation activity.

There are two factors, which define most of the reactions in the organic chemistry^{9,14,15}: the interaction between the charges and the orbital correlation. Most reactions run under orbital control. On the other hand, in many reactions the relative reactivity of the centers depends on the attacking reagents and on other conditions. It may be due to Van der Waals interactions within and between the molecules and especially their steric configuration¹⁶⁻¹⁸.

The molecular structure of DBPC and HPAN are presented in Fig. 1. Molecular simulation results show that in DBPC the -OH group is steric hindered by *tert*-butyl groups. The result is something like a protective shield and the -OH group cannot take a coplanar position with the aromatic nucleus. As a result of the O-effect of the *tert*-butyl groups the aromatic nucleus is not completely planar and the -OH group is nearly perpendicular to the aromatic nucleus. This screening of the -OH group makes it hardly accessible for the Van der Waals interactions. Our simulation results in agreement with Georgiev and Karamancheva⁹. In HPAN the -NH group also can't take a coplanar position with the aromatic nucleus. The aromatic nucleus and the octyl are not planar.

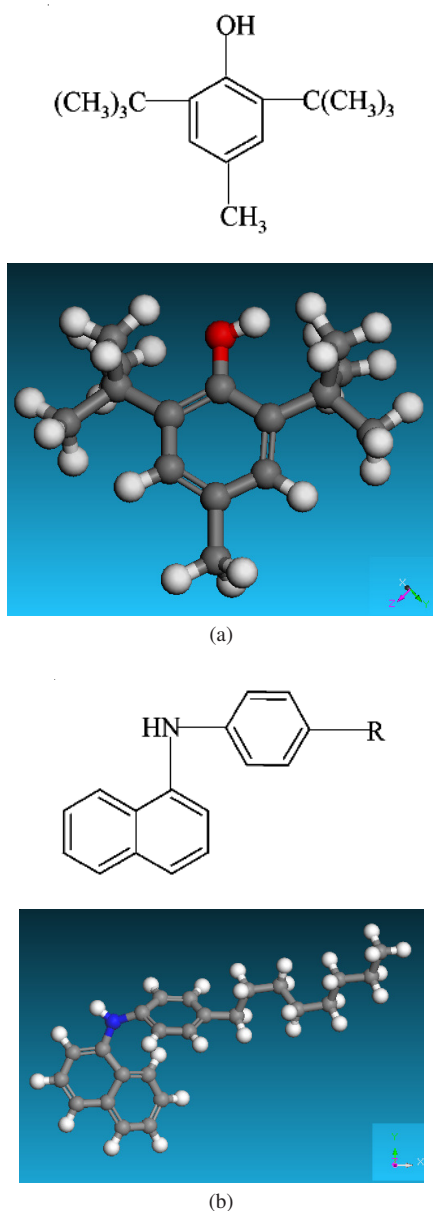


Fig. 1. Plane structure of (a) DBPC and (b) HPAN

Model mixture of DBPC and HPAN has been investigated, as is shown in Fig. 2. Initially it is suggested that the hydrogen bond was formed as a result of the mixing of the two antioxidants. Hydrogen bonding will influence not only the O-H vibration frequency but also the N-H vibration to which it

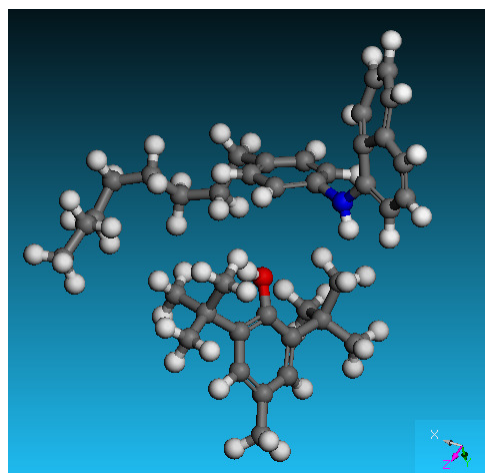


Fig. 2. Molecular modeling space structure of DBPC and HPAN

hydrogen bonds. All kinds of rotation of the molecular diagrams and of molecular models show that the -NH and -OH groups cannot come as close as 4-5 Å in order to perform van der Waals interactions if the two cycles are coplanar, the distances are longer than the length of the hydrogen bond, which is 1.6-1.7 Å⁹. Thus, there is no hydrogen bond exist in the compounds of DBPC and HPAN. Fig. 3 is the FT-IR spectra of DBPC, HPAN and a mixture of DBPC:HPAN in a mass proportion of 1:1. Characteristic peak for the -OH group of DBPC is at 3650 cm⁻¹. Characteristic peak for the -NH group of HPAN is at 3413 cm⁻¹. Fig. 3 indicates that the spectrum of mixtures of DBPC and HPAN at 3650 cm⁻¹ -OH, 3413 cm⁻¹ -NH, 2950 cm⁻¹ -CH₃ vibration frequencies *et al.*, are the addition of DBPC spectrum and HPAN spectrum¹⁵. The spectra in Fig. 3 present that there is only a mechanical mixture of DBPC and HPAN and there is no interaction between them.

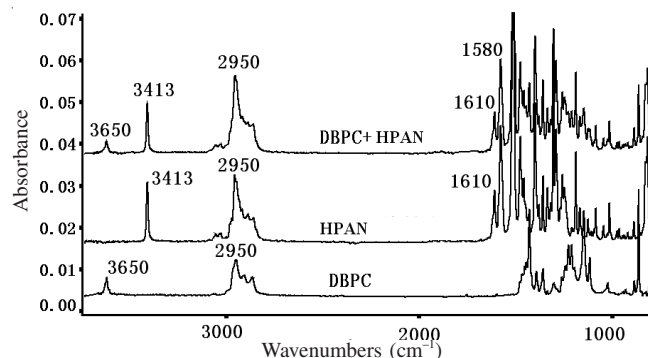


Fig. 3. FT-IR spectrum of DBPC, HPAN and a mixture of DBPC and HPAN in mass proportion of 1:1 at 27 ± 1 °C

Upon raising the temperatures, no chemical reaction occurs between the two compounds. This was also confirmed by present experiments by the help of FT-IR spectroscopy. DBPC and HPAN were heated at 110 °C, the composite antioxidant were heated at 90 and 110 °C. All samples turned into liquid after 20 min heat treatment. The samples (cooled to room temperature) heated for different time were tested by FT-IR spectroscopy. The spectra are shown in Figs. 4-9.

Fig. 4 presents the characteristic peak for the -OH group of DBPC at 3650 cm⁻¹ become wider appreciably than initialization after heated 600 h because of decomposition and other

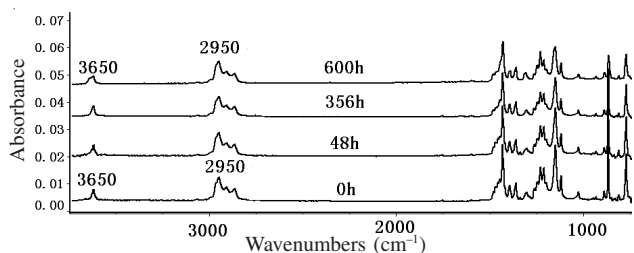


Fig. 4. FT-IR spectroscopy of DBPC heated at 110 °C

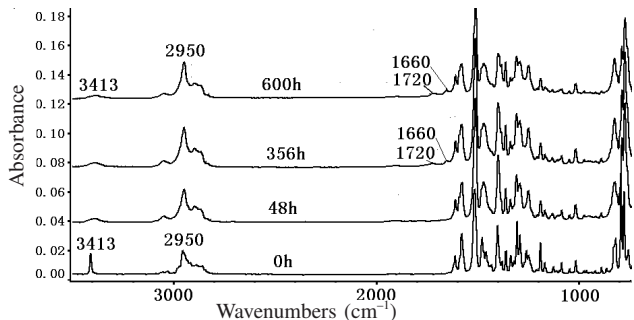


Fig. 5. FT-IR spectroscopy of HPAN heated at 110 °C

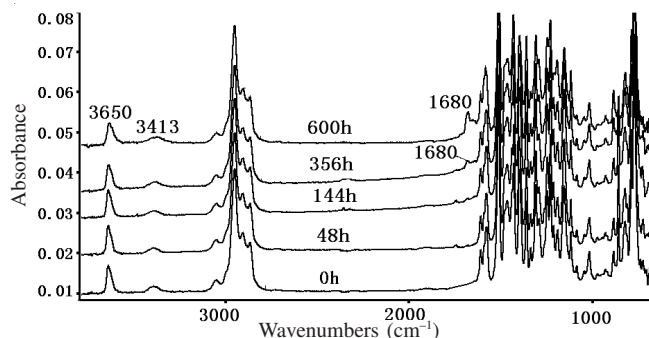


Fig. 6. FT-IR spectroscopy of the composite antioxidant heated at 90 °C

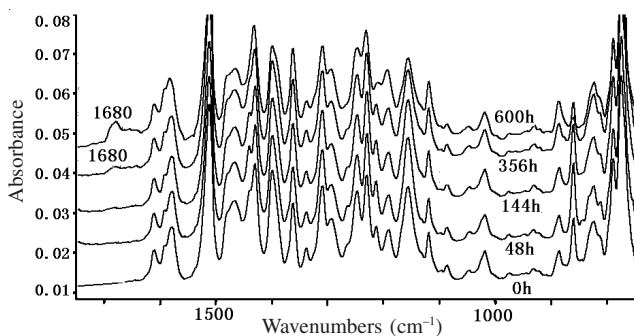


Fig. 7. Back enlargement FT-IR spectroscopy of the composite antioxidant heated at 90 °C

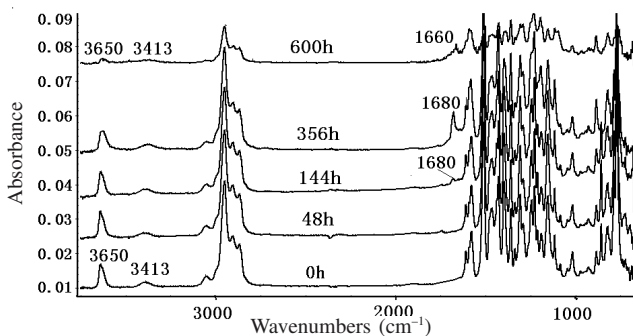


Fig. 8. FT-IR spectroscopy of the composite antioxidant heated at 110 °C

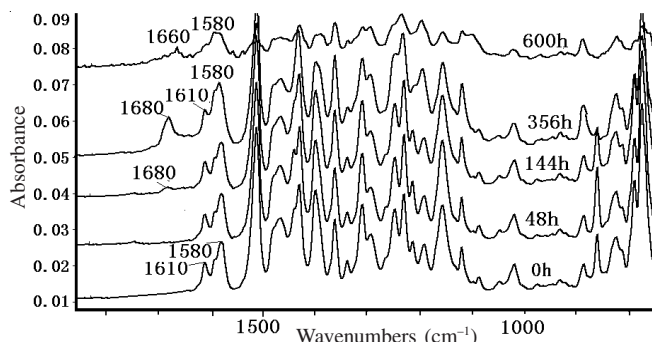


Fig. 9. Back enlargement FT-IR spectroscopy of the composite antioxidant heated at 110 °C

absorption bands of DBPC also have a little attenuation during the heat treatment. HPAN is powder at natural state. However, it become liquid when heated and the HPAN samples heated for different time are all liquids when cooled down to room temperature. From Fig. 5, it can be seen that the spectrum of HPAN powder and HPAN liquid are totally different. This phenomenon was caused by different state of HPAN. The HPAN spectrum shows two new absorption bands after heating 356 h at 1660 and 1720 cm^{-1} during the heat treatment. In addition, characteristic absorption band of HPAN at 3413 cm^{-1} becomes a little wider because of decomposition and other absorption bands of HPAN have a little attenuation as the same as DBPC.

The spectra of the mixture composed of DBPC and HPAN in a mass proportion of 1:1 at 90 and 110 °C are shown in Figs. 6-9. At 90 °C, the absorption bands at 3650 and 3413 cm^{-1} becomes wider with increasing heating time. There appears a new absorption band at 1680 cm^{-1} after 356 h and it becomes much stronger after 600 h heat treatment (Figs. 6 and 7).

The higher the temperature, the faster speed of material may changes. At 110 °C, there also appears a new absorption band at 1680 cm^{-1} only after heating 144 h. However, the new absorption band at 1680 cm^{-1} become nearly unclear after 600 h and the absorption bands at 3650 and 3413 cm^{-1} also become wider first and then nearly disappear after 600 h heat treatment (Fig. 8 and Fig. 9). This is because of the decomposition of HPAN at higher temperature.

From the FT-IR spectra of DBPC, HPAN and a mixture of DBPC:HPAN in a mass proportion of 1:1 during heat treatment, it is observed that there is no new absorption band appearing in DBPC spectroscopy during heat treatment. There is two new absorption bands at 1660 and 1720 cm^{-1} appearing in HPAN spectrum because of itself oxidation and there only one new absorption band at 1680 cm^{-1} appears in mixture spectroscopy. Mixture molecular simulation shows that there is no interaction between DBPC and HPAN. In the mixture of DBPC and HPAN, the concentration of HPAN is 50 %. The low concentration of HPAN can lead to the blue shift or red shift of the absorption band at 1660 and 1720 cm^{-1} . Thus, the absorption band at 1680 cm^{-1} is produced by HPAN. DBPC and HPAN can't react with each other and no new materials are formed which can have antioxidant effect. Thus, it is the synergistic antioxidant effect of DBPC and HPAN that improves the new insulation oil oxidation stability significantly.

Synergistic mechanism of the composite antioxidant in the new insulation oil: The oxidation onset temperature of new insulation oil added the composite antioxidant is 217 °C, which is 22 °C higher than new insulation oil with no composite antioxidant added and 16 °C higher than transformer oil. The synergistic antioxidant effect of DBPC and HPAN improves the new insulation oil oxidation stability obviously. However, at the present moment there exists no common and therefore simple theory, which could account for the intermolecular interactions^{9,14,17}. For this reason it is difficult to explain the synergetic effect between DBPC and HPAN. It is possible that: (1) HPAN is amine antioxidant which can react with the acids generated during the oil oxidation, then reduce the catalyze effect of acids in the process of oil oxidation; (2) DBPC and HPAN are both chain breaking radical scavengers, they can all react with radicals in the insulation oil to form stable compounds and prevent propagation of the oil oxidation; (3) the octyl groups in HPAN is very long (Fig. 2), it can surround other molecule and provide a protect ability to molecule of the new insulation oil.

Conclusion

Pressure differential scanning calorimetry can be used to select the antioxidant used in the insulation oil. Pressure differential scanning calorimetry results show that the best composite antioxidant in the new insulation oil is 0.3 % DBPC + 0.3 % HPAN. The composite antioxidant can improve the new insulation oil oxidation stability significantly. The composite antioxidant makes the oxidation onset temperature of the new insulation oil 22 °C higher than new insulation oil with no composite antioxidant added and 16 °C higher than new mineral oil.

Molecular simulation results present that there is no hydrogen bond exists in the compounds of DBPC and HPAN. There is only a mechanical mixture of DBPC and HPAN and there is no interaction between them.

During heat treatment, FT-IR spectra show that there is no new absorption band appearing in spectroscopy of DBPC, two new absorption bands at 1720 and 1660 cm⁻¹ appear in HPAN spectra. The mixture of DBPC and HPAN only appears

a new absorption band at 1680 cm⁻¹. DBPC and HPAN can't react each other and neither produce new materials which can have antioxidant effect. It is the synergistic antioxidant effect of DBPC and HPAN that improves the new insulation oil oxidation stability significantly.

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