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Decomposition of Transformer Oil Under Ultrasonic Irradiation During Degassing Process

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Abstract: In the degassing process of transformer oil with ultrasonic waves, decomposition of the oil was observed. Light hydrocarbons, including methane, ethane, ethylene, acetylene, propane *etc*, were found to be released continuously from the oil into headspace within a closed vial placed in an ultrasonic field. The gases came from decomposition of hydrocarbon molecules under cavitation effect.

Keywords: Transformer oil, ultrasonic cavitation, degassing, decomposition.

Analysis of dissolved gases in transformer oil is widely performed by electrical utility industries for routine performance monitoring. From the variations in the concentrations of these gases, they can diagnose the presence of faults at an early stage and take preventive action before failures occur. These 'fault gases' include mainly the following: carbon dioxide, carbon monoxide, hydrogen and light hydrocarbons (*e.g.* methane, ethane, ethylene, acetylene and propane). Standard laboratory methods include: vacuum gas extraction method approved by ASTM D3612, gas stripping method in Europe[1, 2] and static headspace method in China (GB 7252-87). They are different mainly in the gas-extracting step but all use gas chromatograph (GC) to quantify components in the gas mixture. In addition to the above methods, ultrasound was reported to help degassing transformer oil [3, 4, 5]. However, it was found that light hydrocarbons, including methane, ethane, ethylene, acetylene and propane, were released from the oil in large amount when exposed to ultrasound. We suspected that if the oil itself were decomposed in the ultrasonic irradiation. The intention of this paper was to investigate the ultrasonic effect on transformer oil during its degassing process.

Experimental

Degassing transformer oil was done within an ultrasonic cleaning tank (50 kHz, 35 watt, Shanghai Branson Ultrasound Ltd., Shanghai). 20 mL transformer oil in a 30 mL glass vial sealed with silicon rubber was suspended closely above one vibrator. 100 μL sample of gas taken from the headspace at the same intervals was injected into a chromatograph (GC-8820, Shanghai Analytical Instrument Factory, Shanghai) equipped

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with a FID detector. Analyzing dissolved-gas (light hydrocarbons) in the liquid phase in the vial was performed by injecting oil sample onto the packing of the column to detect volatile components.

A static headspace gas chromatographic method on basis of the Henry's Law was used to analyze gas components in the oil. In the experiment, 30 mL oil sample in a 40 mL vessel was stirred for 3 hours with a magnet stirrer and circulated with water bath of 70℃ after the vessel was sealed. Then dissolved gases in oil reached an equilibrium between the oil and its gas phase. Gas mixture in the headspace was measured with GC.

Identification and calibration of light hydrocarbons were performed with a standard gas mixture of CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6 and *n*, *i*-C_4H_{10} (State Key Laboratory of Catalysis of Dalian Institute of Chemical Physics, CAS, Dalian).

Results and Discussion

In the preliminary experiment, when the oil from an in-service transformer was degassed by ultrasound, light hydrocarbons were released continuously from the oil and their concentrations increase to high values (see **Figure 1)** in the testing period. This is unusual, because the concentrations of dissolved gases in insulating oil of a normally operating transformer should not be so high. To search for the source of these gases, the blank oil (containing almost no gas species in the oil, prepared by similar method described in details in Annex A1 of ASTM D3612-96) was examined with the same ultrasound. The similar phenomenon was observed: a great deal of CH_4, C_2H_4, C_2H_6, C_2H_2, C_3H_6, C_3H_8, *etc*. were produced into headspace as shown in **Figure 1**. When the experiment was completed, gases in the oil were analyzed by directly injecting the oil onto the head of GC column and the chromatogram was shown in **Figure 2**. However, injection of the same volume (20 μL) of blank oil (containing neglectable gas species) did not show any peaks (not shown). Likewise, analysis of gases in blank oil with the static headspace method showed no peaks in the chromatogram (not shown).

Figure 1 Concentrations of gases in headspace above the blank oil in a sealed vial irradiated with ultrasonic waves

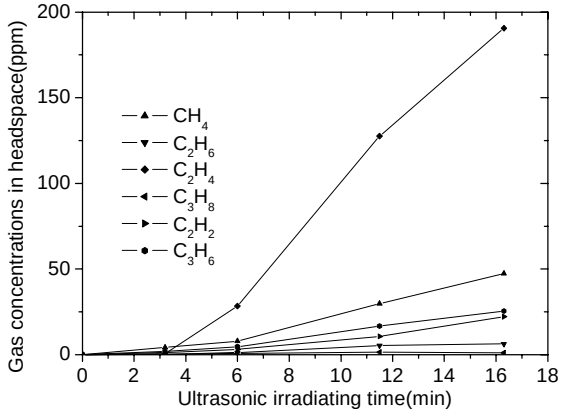
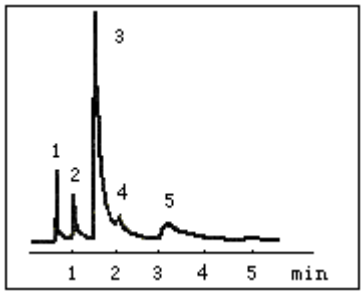


Figure 2 Chromatogram of analysis of dissolved gases in newly irradiated blank oil with ultrasound (50 kHz, 35 watt)



1. CH_4, 2. C_2H_6, 3. C_2H_4, 4. C_3H_6, 5. C_2H_2

According to the above experiments, the blank oil did not contain light hydrocarbons and the insulating oil was decomposed under the ultrasonic irradiation during its degassing process. Light hydrocarbons were among the products of its degradation.

How does this case happen? Ultrasonic degassing, according to literature[6, 7], begins from the formation of cavitations in the medium. As the ultrasonic waves at suitable frequency and intensity are propagated through a liquid, due to the oscillations of the particles of the medium, regions of compression and rarefaction are formed. At suitable frequency and intensity of ultrasonic irradiation, a large amount of very small bubbles in microns can be created in the rarefaction regions (cavitation phenomenon). Study shows that these small bubbles can be stable or transient. Stable bubbles together with the other remaining small gas bubbles in the liquid tend to grow and coalesce into larger bubbles and rise to the surface. On the other hand, transient bubbles would expand and collapse violently in high frequency alternating pressure of the sound field, thereby causing very high momentary local temperature and pressure, the maximum value as high as 4200 K and 9.88×10^7 Pa, respectively. Free radicals may be created in the period, thus initiating degradation of other compounds[8]. Still further, from the reports, we know that CCl_4[9], $CHCl_3$, CH_2Cl_2, benzene[8], acenaphtylene[10] and decane can be degraded by ultrasound. As to benzene, C_2H_2 was one of the sonication products of benzene[11]. So we think that both aromatic molecule and the other hydrocarbon molecules in the transformer oil may be broken up under the high temperature and pressure caused by ultrasonic irradiation.

It happens to be that decomposition of transformer oil because of aging or faults happened within transformer also produces such gases as CH_4, C_2H_4, C_2H_6, C_2H_2, C_3H_6 and C_3H_8. In this case, degassing and decomposing gases produce together.

Conclusion

From the above experiments, it can be concluded that degassing of transformer oil by using ultrasonic irradiation should be avoided, because the severe conditions might cause cavitation effect, which would lead to false results. Although ultrasonic irradiation is

unsuitable to serve the analysis of the dissolved gas in insulating oil, however it may use in the environmental science for degradation of hydrocarbons such as benzene contained in water.

References

1. Y. Leblane, R. Gilbert, M. Duval, J. Hubert, *J.Chromatog.*, **1993**, *633*, 185.
2. J. Jalbert, R. Gilbert, P. Tetreault, *Anal. Chem.*, **2001**, *73*, 3328.
3. R. L. Ma, D. Z. Li, *12's National Conference on Chromatographia*, *vol. 2*, 470, Hangzhou, China, **1999**.
4. W. Kimiji, A. Takayuki, *JP 57119717*, **1984**.
5. J. Jalbert, *Hewlett Packard Application Note* 228, October, **1995**.
6. B. Brown, *High-intensity Ultrasonics Industrial Applications*, Iliffe Books Ltd, London, **1965**.
7. H. F. Mark, D. F. Othmer *et al*, *Kirk-Othmer Encyclopedia of Chemistry Technology*, John Wiley & Sons, Inc. , USA, *vol. 23*, 3rd edition, p. 462.
8. C. Wei, *Shanghai Environmental Science*, **1999**, *18*, 457.
9. I Hua, M. R. Hoffman, *Environmental Science and Technology*, **1996**, *30*, 846.
10. E. Leonhardt, R. Stahl, *Anal.Chem.*, **1998**, *70*, 1228.
11. R. Feng, *Sonochemistry and its Applications (Chinese)*, Anhui Science and Technology Press, Hefei, China, **1992**, 238.

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