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STUDY OF RADIATION-CHEMICAL DECOMPOSITION OF TRANSFORMER OIL BY THE METHOD OF IR-SPECTROSCOPY

Z.I. Iskenderova

Institute of Radiation Problems of ANAS
zenfira_iskenderova@mail.ru

Abstract: Herein, it has been studied the IR absorption spectra of γ - irradiated samples of fresh transformer oil T - 1500, depending on the absorbed dose using IR spectroscopy. Stretching vibrations =C-H, plane deformation vibrations –C=C and out-of-plane deformation vibrations –CH of aromatic compounds are observed in the IR - spectra. In addition, stretching vibrations –C-H and deformation vibrations –C-CH_3 (antisymmetric and symmetric) are observed in alkanes. It has been established that IR absorption spectra are observed in the range of $\Delta\lambda_1 = 2800 - 3300\ cm^{-1}$, $\Delta\lambda_2 = 2000\ cm^{-1}$, $\Delta\lambda_3 = 1350 - 1450\ cm^{-1}$ and $\Delta\lambda_4 = 600 - 1200\ cm^{-1}$. The absorption band $\Delta\lambda_4 = 600 - 1200\ cm^{-1}$ is the diffuse part of the spectrum, including a number of weak absorption bands.

Key words: transformer oil, γ-radiation, IR- spectroscopy

1. Introduction

The problems, associated with the radiation resistance of materials of electrical equipment arising from various emergency situations are investigated in many works devoted to the determination of the performance of various components and assemblies of nuclear power plants [1]. The issues became especially relevant after the accident of the Chernobyl nuclear power plant in 1986. After the accident of the Chernobyl nuclear power plant, a number of accidents were identified with a level higher than INES 4 (International Nuclear Events Scale) [2].

The most functionally important component materials and electrical equipment - transformer oil and electrical insulating cardboard have been investigated in the works of [3, 4, 5] in order to determine the possible reduction in reliability, in particular, transformers as a result of accidental exposures.

Irradiation of such a complex system as transformer oil leads to the absorption and redistribution of radiation energy between the oil components. It is impossible to follow completely the possible chemical changes occurring in the irradiated systems. Therefore, the individual components, both sulphuric and aromatic compounds, isolated from transformer oil have been studied in some works [6-9].

In this paper, it has been investigated the IR absorption spectra of the samples of fresh transformer oil T-1500 at different absorbed doses by the method of IR Spectroscopy.

2. Irradiation methods

It has been used the fresh transformer oil T-1500, the production of the oil refinery plant named after H.Aliyev in Azerbaijan.

The IR absorption spectra of the samples were recorded on a Fourier - Spectrometer of the Varion 640 IR brand in the wavenumber region of $\nu = 3600 - 400\ cm^{-1}$.

The spectra of the samples irradiated at different doses were taken under the same conditions as thin films between two KRS-5 plates. The relative intensities (J_{max}/J_0) of the absorption bands were calculated and their dose dependences were obtained, where J_0 and J are the intensities of the absorption bands of the non-irradiated and γ-irradiated samples, respectively.

Irradiation of oil samples was performed under the influence of γ-radiation from the ^{60}Co isotope under the static conditions at room temperature in 15 ml glass ampoules containing 5 ml of oil. The absorbed dose rate was 0.21 Gy/s.

3. Results

IR absorption spectra of transformer oil have been shown in Fig. 1.

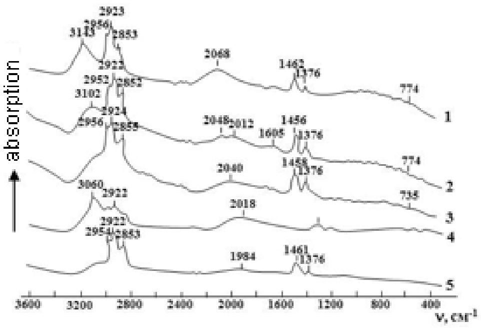

Fig.1. IR absorption spectra of transformer oil irradiated at different doses: 1– initial; 2 – 4.18 kGy; 3 – 27.48 kGy; 4 – 68.48 kGy; 5 – 136.8 kGy. Irradiated by γ- $radiation$ at different doses in the range of 4-136.8 kGy.

As it can be seen from fig. 1 (1), IR absorption spectra are observed in the range of $\Delta\lambda_1 = 2800 - 3300\ cm^{-1}$, $\Delta\lambda_2 = 2000\ cm^{-1}$, $\Delta\lambda_3 = 1350 - 1450\ cm^{-1}$ and $\Delta\lambda_4 = 600 - 1200\ cm^{-1}$. The absorption bands in the region of $\Delta\lambda_1$, $\Delta\lambda_2$, $\Delta\lambda_3$ are quite clearly counted.

Figure 1. (2-5) shows the absorption spectra of samples irradiated at doses of 4-136.8 kGy. As it is seen, a change in the intensity of the bands with increasing dose is observed in all absorption regions, and the nature of the change depends on the type of components.

The absorption band $\Delta\lambda_4 = 600 - 1200\ см^{-1}$ is the diffuse part of the spectrum, including a number of weak absorption bands [10]. The identified absorption bands are shown in Table 1. As it is seen, stretching vibrations =C–H, plane deformation vibrations –C=C and out-of plane deformation vibrations –CH of aromatic compounds are observed in the spectra. In addition, stretching vibrations –C–H and deformation vibrations –C–CH_3 (antisymmetric and symmetric) are observed in alkanes.

Table 1.

Identified absorption bands.

№	λ_{max}, cm^{-1}, experimental	λ_{max}, cm^{-1} [8]	Vibration
1	3143	3030-3080	Stretching vibration =C-H in aromatic compounds
2	2956 2923 2853	2962 2926 2872 2853	Stretching vibration C-H in alkanes

3	2068 2048 2040 1984	2000-1600	Substituted aromatic compounds in the range of 2000-1650$см^{-1}$.
4	1605 Wide blurred spectrum	1600–1500	Plane deformation vibration of aromatic compound C=C
5	1462 1376	1450 1380-1370	Deformation vibrations in alkanes C-CH_3 (antisymmetric) and C-CH_3 (symmetric
6	774; 735; 774 etc. Wide blurred spectrum	770-730 760-690 810-750 770-715	Out-of-plane deformation vibration of aromatic compounds CH

Fig. 2. shows the change in the intensity of the bands J_{max} / J_0 depending on the absorbed dose. As you can see, the value of J_{max}/J_0 for bands with λ_{max}=3143 cm^{-1}, 2068 cm^{-1} and 774 cm^{-1} decreases with initial doses (up to 4 kGy), then increases with increasing doses up to 68.4 kGy. A further increase in the dose leads to a decrease in the value of J_{max} / J_0. As it is indicated above, these absorption bands are characteristic of aromatic hydrocarbons.

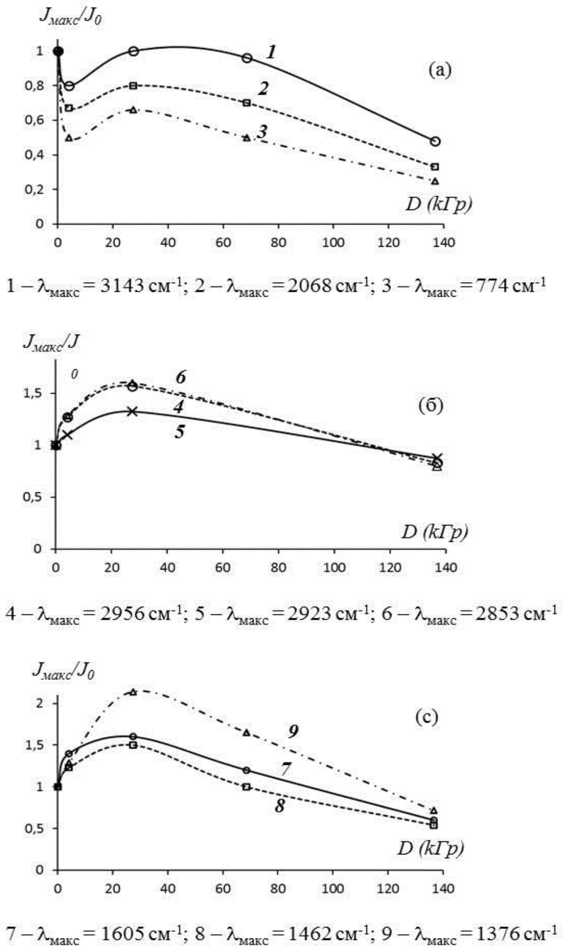

Fig. 2. The relative intensity of the respective absorption bands at different absorbed doses (4-136.8 kGy).

Unlike aromatic hydrocarbons, the intensity of the bands characteristic of alkanes increases up to the dose of 68.4 kGy, then decreases with increasing dose.

4. Discussion of the Results

Transformer oil has a complex hydrocarbon composition and contains the following main components: paraffins 10-15%, naphthenes or cycloparaffins 60-70%, aromatic hydrocarbons 15-20%, asphalt-resinous substances 1-2%, sulfur compounds <1%, nitrogen compounds <0.8%, naphthenic acids <0.02%, antioxidant additive (ionol) <0.2-0.5% [11]. The main characteristics of the oil T-1500 are shown in table 2.

Table 2.

Key indicators of T-1500

The name of indicators of **T-1500**	Norm according to GOST (TU)
Kinematic viscosity, mm^2/s at a temperature of 50°C	8
Density at 20°C, kg/m^3, not more	0.885
Sodium sample, optical density, not more	0.4
Acid number, mg KOH/g	0.01
volatile low molecular weight acid, mg KOH/g	0.04
acid number, mg KOH/g	0.2
Tangent of dielectric loss angle at 90°C,%, not more	0.5
Color, units of CNT, not more	1.5

When transformer oil is irradiated, the energy of ionizing radiation is absorbed in proportion to the electron dose of each component. Since the main components of the oil are alkanes, cycloalkanes, and aromatic hydrocarbons, the energy is mainly absorbed directly by the molecules of these compounds.

The radiolysis of the main components of transformer oil has been studied in some detail by using pulsed radiolysis methods with electrical and optical recording and by determining stable products. The main products of n-hexane radiolysis are C_6H_{13}, C_4H_9, C_3H_7, C_2H_5, CH_3 radicals and cyclohexane is cyclo-C_6H_{11}. The total radiation-chemical yields of radicals are 5-6 particles / 100 eV. The main molecular product of the radiolysis of hexane is molecular hydrogen, in addition, hexene-1, hexene-2 (cis-trans) and dodecanese (G> 0.5 molecules/100 eV) are formed in large yields.

The main products of cyclohexane radiolysis are also molecular hydrogen, and cyclohexene and dicyclohexyl are formed with noticeable yields (G ~ 2-3molecules/100eV). Unlike hexane and cyclohexane, aromatic hydrocarbons are characterized by high radiation resistance. The hydrogen yield in the radiolysis of benzene is only G = 0.039 molecules / 100 eV. The formation of polymer products occurs more efficiently with G = 1.1 molecules/100 eV [12].

During the radiolysis of a complex system, the spectra and the yields of radiolysis products change due to the possibility of transferring electronic excitation energy and charge. The molecules of hexane, cyclohexane, and benzene have an ionization potential of 10.4; 9.9 and 9.2 eV. [13]. A comparison of the ionization potential indicates the possibility of charge transfer from the “mother” ions of hexane and cyclohexane to the benzene molecules. Benzene molecules also more efficiently capture the hydrogen atoms and hydrocarbon radicals. In addition, the transfer of electronic excitation from alkane and cycloalkane molecules to benzene molecules is possible, since they have higher energy electronic states. For example, the energy of the singlet state of hexane molecules is 9.13 and 9.84 eV [13]. The chemical processes are carried out to the formation of gaseous products such as H_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}.

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ИССЛЕДОВАНИЕ РАДИАЦИОННО-ХИМИЧЕСКОГО РАЗЛОЖЕНИЯ ТРАНСФОРМАТОРНОГО МАСЛА МЕТОДОМ ИК-СПЕКТРОСКОПИИ

З.И.Искендерова

Резюме: В данной работе исследованы ИК-спектры поглощения γ - облученных образцов свежего трансформаторного масла Т-1500 в зависимости от поглощенной дозы методом ИК- спектроскопии. В ИК – спектрах наблюдаются валентные колебания =C-H, плоскостные деформационные колебания –C=C и вне плоскостные деформационные колебания –CH ароматических соединений.

Кроме того, наблюдаются валентные колебания –C-H и деформационные колебания –C-CH_3 (антисимметричных и симметричных) в алканах. Установлено, что ИК-спектры поглощения наблюдаются в диапазоне $\Delta\lambda_1 = 2800 - 3300\ см^{-1}$, $\Delta\lambda_2 = 2000\ см^{-1}$, $\Delta\lambda_3 = 1350 - 1450\ см^{-1}$ и $\Delta\lambda_4 = 600 - 1200\ см^{-1}$. Полоса поглощения $\Delta\lambda_4 = 600 - 1200\ см^{-1}$ представляет собой размытая часть спектра, включающей ряд слабых полос поглощения.

Ключевые слова: трансформаторное масло, γ-излучение, ИК-спектроскопия

TRANSFORMATOR YAĞININ İQ-SPEKTROSKOPİYA METODU İLƏ RADİASİYA-KİMYƏVİ PARÇALANMASININ TƏDQİQİ

Z.İ. İskəndərova

Xülasə: Bu işdə İQ spektroskopiya metodu ilə müxtəlif udulma dozalarında T-1500 təzə transformator yağı nümunələrinin İQ udulma spektrləri tədqiq edilib. İQ-spektrlərdə aromatik birləşmələrin valent rəqsləri =C-H, müstəvi deformasiya rəqsləri –C=C və qeyri müstəvi deformasiya rəqsləri –CH müşahidə edilir. Bundan başqa (asimmetrik və simmetrik) alkanlarda valent rəqsləri –C–CH_3 müşahidə edilir. İQ udulma spektrlərinin $\Delta\lambda_1 = 2800 - 3300\ sm^{-1}$, $\Delta\lambda_2 = 2000\ sm^{-1}$, $\Delta\lambda_3 = 1350 - 1450\ sm^{-1}$ və $\Delta\lambda_4 = 600 - 1200\ sm^{-1}$ intervalında müşahidə edildiyi təyin olunmuşdur. Zəif udulma zolağı $\Delta\lambda_4 = 600 - 1200\ sm^{-1}$ bir sıra udulma zolaqları daxil olan, spektrin yayılmış hissəsindən ibarətdir.

Açar sözlər: transformator yağı, γ - şüalanma, İQ spektroskopiya